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THE CAUSE AND PREVENTION OF CALCIUM SULPHATE SCALE IN STEAM BOILERS

A REPORT OF AN INVESTIGATION

CONDUCTED BY

THE ENGINEERING EXPERIMENT STATION
UNIVERSITY OF ILLINOIS

IN COÖPERATION WITH

THE UTILITIES RESEARCH COMMISSION, INC.

BY

FREDERICK G. STRAUB

BULLETIN No. 261
ENGINEERING EXPERIMENT STATION
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ENGINEERING EXPERIMENT STATION

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FREDERICK G. STRAUB
SPECIAL RESEARCH ASSISTANT PROFESSOR OF CHEMICAL ENGINEERING

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Calcium sulfate
Feed water

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THE CAUSE AND PREVENTION OF CALCIUM SULPHATE SCALE IN STEAM BOILERS

I. Introduction

1. *Purpose of Investigation.*—The results of the investigation conducted to determine the cause and methods of prevention of embrittlement in steam boilers emphasized the importance of maintaining a definite sulphate concentration in the boiler water. The American Society of Mechanical Engineers' Boiler Code Committee in 1932 made the following recommendation:

"Operating evidence supplemented by laboratory work indicates that if not less than the following ratios of sodium sulphate to total sodium hydroxide and sodium carbonate alkalinity calculated to equivalent sodium carbonate are maintained in the boiler water, 'caustic embrittlement' will be inhibited:

Working pressure of boiler lb. gage	Sodium sulphate		Total sodium hydroxide and carbonate alkalinity calculated to equivalent sodium carbonate
0 to 150*	1	to	1
150 to 250	2	to	1
250 and over	3	to	1

Within recent years there has been much discussion as to the possibility of maintaining the desired sulphate ratios without causing calcium sulphate scale formation, especially at the higher steam pressures. Thus Hall† states:

"The formation of adherent anhydrite scale on the evaporating surfaces of a boiler operating at 185 deg. cent. (150 lb. gage pressure) is prevented by using soda ash to maintain the following conditions in the boiler water:

$$CO_2 \text{ p.p.m.}‡ > 0.0883\ SO_4 \text{ p.p.m.}$$

It is evident from the expression

$$CO_3 > K \text{ (at operating pressure } p) \times SO_4$$

that the maintenance of scale-free conditions depends upon keeping a definite supply of CO_3 in the boiler water. In case conditions arise such that the necessary CO_3 concentrations cannot be maintained, then it is no longer feasible to use soda ash as the conditioning chemical. . . . Thus higher operating pressures are characterized by more rapid decomposition of CO_3 and at the same time by the necessity for maintaining higher CO_3 concentration, as the value of K is greater at higher than at lower operating pressures. . . .

"A satisfactory and practical answer to the complete conditioning of water for high-pressure operation may be given as follows: If the make-up water is

*For cases where this ratio should be higher, see Bulletin No. 216 of the Engineering Experiment Station, University of Illinois, entitled "Embrittlement in Boilers," 1930, pp. 76-78.

†Bulletin 24, Carnegie Institute of Technology, 1927.

‡p.p.m. is abbreviation for parts per million and is a standard method of reporting concentration in boiler waters.

evaporated, and the only impure water entering the boiler consists of the condenser leakage, then conditioning the boiler with phosphate is the only chemical control necessary. If the make-up water is not evaporated, and is of some magnitude, then economy may demand a pretreatment (with lime and soda ash for any water, or by a base exchange process if the water does not contain temporary hardness) followed by the final conditioning of the boiler water with phosphate. . . . In any event, however, the final control of the boiler water must be based on the use of a stable substance such as phosphate."

If the A.S.M.E. Boiler Code recommendation for the prevention of embrittlement is followed, the amount of sulphate becomes too high for the carbonate, and scale would be predicted by the older theory. However, in many instances ratios of over 3 are being maintained in plants at higher pressures, calcium is entering the feedwater in various amounts, phosphate is not being added, the amount of CO_3 is decidedly low, and yet scale is not a problem.

According to existing theories, these plants should form scale. However, with the boilers operating at a pressure even as high as 700 lb. per sq. in., with calcium present in varying amount, the operators do not experience scale troubles.

These discrepancies between theory and actual operating conditions may be readily explained on the basis that there are not sufficient data available to formulate theories which hold at the higher pressures. Thus, Hall's figures were calculated by using the solubility product, and without exact values for the solubility of calcium carbonate. His determination of the solubility of calcium sulphate was made only up to about 225 lb. pressure. Partridge* has checked Hall's figures on the solubility of calcium sulphate, but he also stopped at about the same pressure. Neither Partridge nor Hall determined the influence of additional salts on the solubility of calcium sulphate.

In order to postulate any fundamental theory of scale formation and prevention, it is essential that data in regard to the solubility of the calcium salts alone, and in the presence of positive and negative ions, be obtained over the entire pressure range of boiler operation. At the same time, data in regard to the behavior of these chemicals under conditions simulating those of actual operation should also be available. Since few of these data were available, the present investigation was undertaken to obtain the most important items of the necessary information.

2. *Method of Investigation.*—Since fundamental knowledge was to be obtained in regard to the behavior of the calcium salts at the desired temperatures, it was essential that actual solubility determi-

*Engineering Research Bulletin No. 15, University of Michigan, 1930.

nations be made under conditions where equilibrium would be reached. This would involve a study of solubilities of the calcium salts in solutions, both alone, and in the presence of positive and negative ions, over the range between 150 and at least 2000 lb. per sq. in. steam pressure (360 and 640 deg. F.). The behavior of the salts used for treatment at the temperatures and pressures should also be studied.

The results of experiments conducted under equilibrium conditions should serve as a criterion of what may be predicted in actual operation. However, it should also be realized that equilibrium is not always reached in actual boiler operation, and additional tests should be run under conditions paralleling those of actual operation in the laboratory and eventually in operating steam boilers.

In order to obtain these desired data, the investigation was divided into five parts, as follows:

(1) Laboratory solubility studies
(2) Laboratory experiments on the decomposition of sodium carbonate solutions
(3) Scale formation in laboratory boiler
(4) Scale prevention in laboratory boiler
(5) Scale prevention in industrial power plants

It would be well to emphasize at this time that this investigation has been primarily directed towards the study of calcium sulphate scale formation and prevention. No attempts have been made to study the magnesium, silicate, or other types of scales which occur. A research is now being conducted dealing with these other types of scales.

3. *Sponsors of Investigation.*—The material embodied in this bulletin results from a research sponsored at the University during the last three years by the Utilities Research Commission, Inc., representing the following companies:

Commonwealth Edison Company
Middle West Utilities Company
Midland United Company
Public Service Company of Northern Illinois
The Peoples Gas Light and Coke Company

The officers of the Commission were as follows:

President—Mr. W. L. Abbott, Chief Operating Engineer, Commonwealth Edison Company.

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The work has been carried on as Case No. 31 of the Utilities Research Commission, Inc., and has been under the direct charge of a sub-committee of that organization:

Mr. A. D. Bailey, Superintendent of Generating Stations, Commonwealth Edison Company, Chairman.

Mr. M. J. Archbold, Superintendent of Station 5, Public Service Company of Northern Illinois.

Mr. A. E. Grunert, Efficiency Engineer, Generating Stations, Commonwealth Edison Company.

Mr. R. B. Harper, Vice President, The Peoples Gas Light and Coke Company.

Mr. J. M. Lee, Assistant to Vice President, Public Service Company of Northern Illinois.

Mr. E. Mandel, Chemical Engineer, Testing Department, Commonwealth Edison Company.

4. *Acknowledgments.*—The investigation was conducted as part of the work of the Engineering Experiment Station of the University of Illinois, of which Dean M. S. Ketchum was the Director, and is one of the researches in Chemical Engineering conducted under the direction of Dr. D. B. Keyes, Professor of Chemical Engineering.

Acknowledgment is made of the generous assistance and coöperation received from the following companies, who furnished equipment for the high-pressure laboratory boiler:

The Babcock and Wilcox Company, New York City,
The Combustion Engineering Corporation, New York City, and
The Reliance Gauge Column Company, Cleveland, Ohio.

The research work in connection with Part III on the decomposition of sodium carbonate solutions was done by Reinhold F. Larson, Instructor in Mechanical Engineering.

The work in connection with Part IV on the laboratory formation of scale was done by Carroll E. Imhoff as a thesis requirement for his M.S. degree in Chemical Engineering.

The analytical procedures have been devised by Mr. J. W. Nelson, and the analytical work has been under his direction.

The author wishes to express his appreciation of the excellent manner in which these men, and others who have been employed in

doing the more routine work, have assisted him throughout this investigation.

II. Solubility Studies

5. *Apparatus for Tests.*—In order to obtain the desired data, an extremely large number of solubility tests must be made. The procedure in the majority of the previous investigations conducted along this line at lower pressures has involved the operation of a small boiler. Naturally, the results obtained from such tests were few in number, since so much time had to be spent in obtaining equilibrium conditions. The present investigation departed from this former practice in that a large number of small steel bombs were used for the solubility determinations. Four constant-temperature boxes were constructed to hold these bombs. With each box at a different temperature, and with six bombs in each box, twenty-four separate solubility tests were run simultaneously, thus obtaining results much more rapidly than is possible by the older procedure.

Figure 1 is from a photograph of one of the testing bombs completely assembled. The details of construction of the bombs are shown in Fig. 2. Figure 3 shows how the bombs are assembled in the heating box, while Fig. 4 shows three of the heating boxes in the foreground. The boxes were electrically heated by means of resistance wire. Constant temperature was maintained by means of automatic potentiometer temperature regulators. The accuracy of the temperature control was $\pm$ 3 deg. F.

6. *Solubility Tests Run.*—The solubility tests run were as follows:

Solid Added	Chemical in Solution Added
Calcium sulphate	None
Calcium sulphate	Sodium carbonate
Calcium sulphate	Sodium hydroxide
Calcium sulphate	Sodium sulphate
Calcium sulphate	Sodium hydroxide, sodium carbonate, and sodium chloride
Calcium carbonate	None
Calcium carbonate	Sodium carbonate
Calcium carbonate	Sodium hydroxide
Calcium carbonate	Sodium sulphate
Calcium carbonate	Sodium hydroxide, sodium chloride, and sodium sulphate
Calcium sulphate and calcium carbonate	None
Calcium sulphate and calcium carbonate	Sodium carbonate
Calcium sulphate and calcium carbonate	Sodium hydroxide
Calcium sulphate and calcium carbonate	Sodium sulphate
Calcium sulphate and calcium carbonate	Sodium hydroxide and sodium carbonate
Calcium sulphate and calcium carbonate	Sodium hydroxide and sodium sulphate

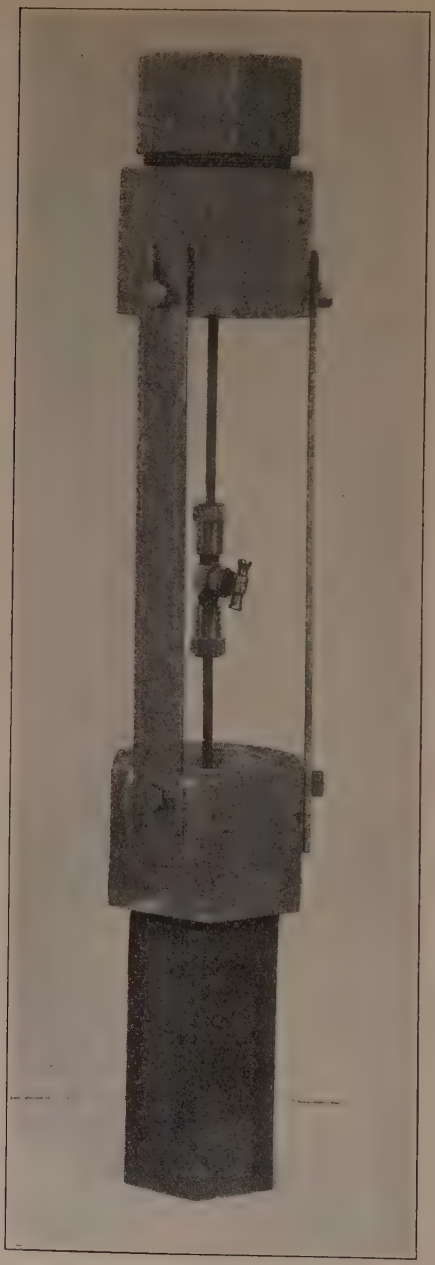

FIG. 1. VIEW OF TESTING BOMB COMPLETELY ASSEMBLED

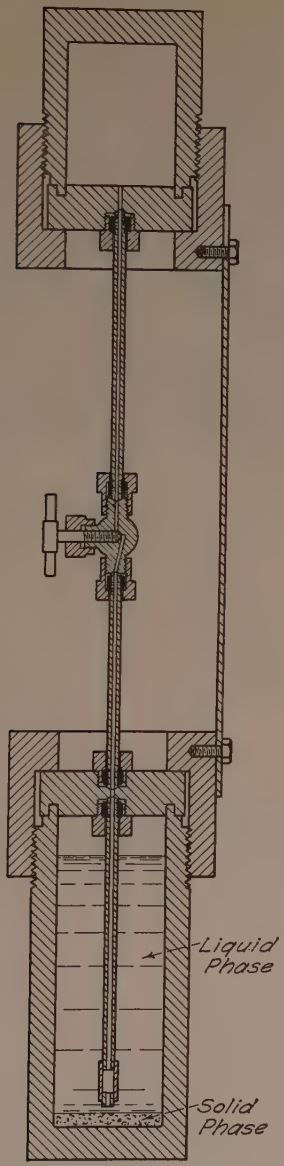

FIG. 2. SECTIONAL VIEW OF TESTING BOMB

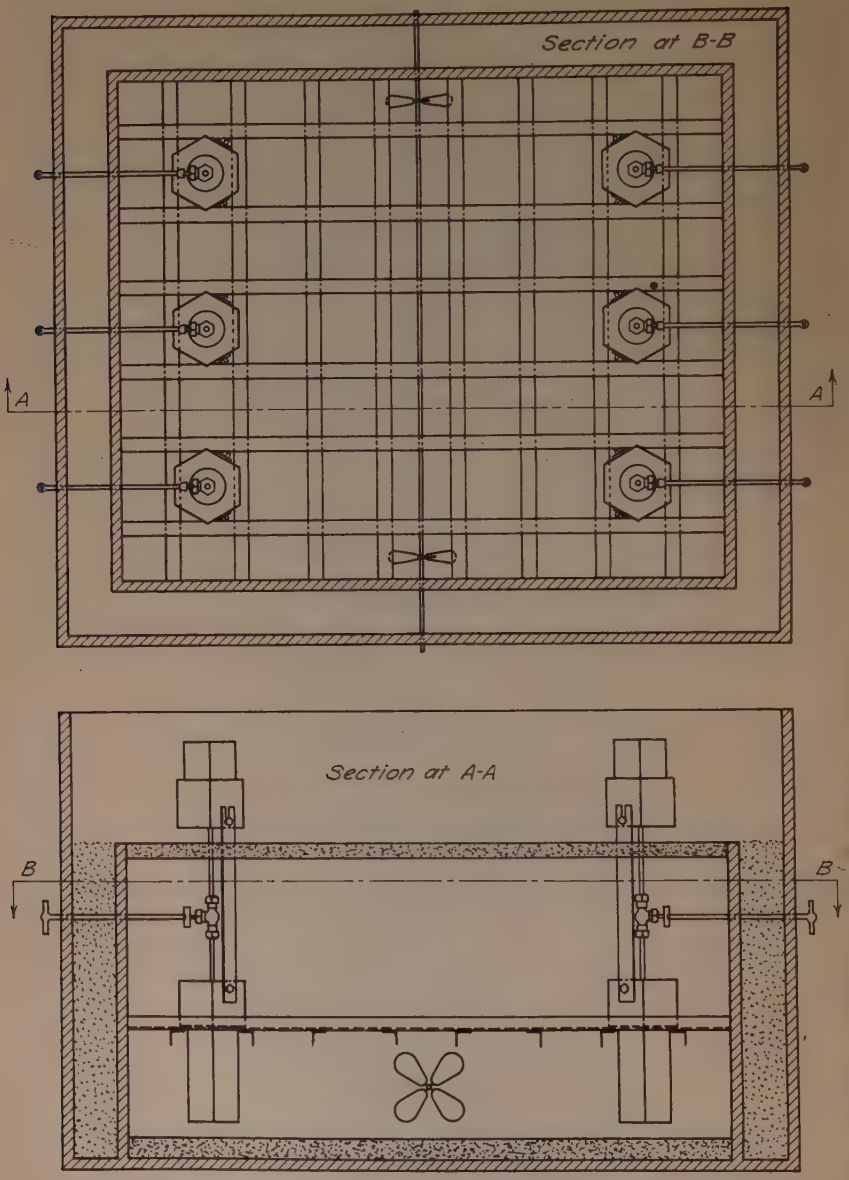

FIG. 3. CONSTANT-TEMPERATURE BOX, SHOWING POSITION OF BOMBS

FIG. 4. VIEW OF LABORATORY, SHOWING THREE OF THE HEATING BOXES IN FOREGROUND

The concentrations of the salts added were as follows:

Sodium hydroxide—0.8 to 60 millimoles* per liter
Sodium carbonate—0.25 to 18 millimoles per liter
Sodium sulphate—0.25 to 18 millimoles per liter
Sodium phosphate—2.5 to 12.5 millimoles per liter
Sodium chloride—2.5 millimoles per liter.

7. *Procedure in Tests.*—The procedure involved in these studies was to put the desired solid phase in the larger or bottom bomb. The desired solution was then added boiling hot, and the bomb closed by screwing on the top. The smaller or top bomb, previously cleaned and closed, was then attached by means of the connections on the capillary copper-lined steel tubing to the lower bomb. The valve between the two bombs was closed. The assembled bombs were put in the heating box and held at the desired temperature until equilibrium was obtained. In these tests the time in the furnace required to reach

*The term millimole per liter is used to express the concentration of the various salts used in this solubility work. A millimole is 0.001 mole. A mole per liter is one gram molecular weight per liter. Thus sodium hydroxide having a molecular weight of 40 would have 40 grams per liter for a concentration of one mole per liter and 0.040 grams per liter for one millimole per liter. To convert from millimoles per liter to parts per million, multiply by the molecular weight; *i.e.*,

millimoles per liter of NaOH $\times$ 40 = p.p.m. of NaOH
millimoles per liter of Na_2CO_3 $\times$ 106 = p.p.m. of Na_2CO_3
millimoles per liter of Na_2SO_4 $\times$ 142 = p.p.m. of Na_2SO_4
millimoles per liter of Na_3PO_4 $\times$ 164 = p.p.m. of Na_3PO_4
millimoles per liter of NaCl $\times$ 58.5 = p.p.m. of NaCl
millimoles per liter of Ca $\times$ 40 = p.p.m. of Ca
millimoles per liter of SO_4 $\times$ 96 = p.p.m. of SO_4
millimoles per liter of CO_3 $\times$ 60 = p.p.m. of CO_3
millimoles per liter of OH $\times$ 17 = p.p.m. of OH

equilibrium was found to be rather short—about 6 to 10 hours. However, the furnaces were run about 90 hours, and, consequently, plenty of time was given for equilibrium conditions to be established.

When it was desired to sample the bombs, the valve was opened by means of the handle extending through to the outside of the heating boxes. After sampling the bombs were removed from the heating box. When cool, the top bomb was removed, the volume of solution accurately measured, and the solution completely analyzed.

The solubility tests reported were run at 360, 405, 470, 540 and 600 deg. F., corresponding approximately to 150-, 250-, 500-, 1000-, and 1500-lb. gage pressure.

The volume of solution added to the bombs at the beginning of the tests was 400 cc. The salts to be used were dissolved in water so as to make standard solutions, and the desired volumes of the standard solutions were added to a volumetric flask and the solution made up to 400 cc. with boiled redistilled water. The solution was then added to the bombs.

The volume of each top bomb was determined by using a standard top having a glass tube in it. The amount of water necessary to fill the bomb to the mark on the tube was determined for each bomb. When the bomb was removed after sampling, the standard top was put on and redistilled water, free from carbon dioxide, was added through the glass tube from a burette. The amount of water added, deducted from the total volume of the bomb, gave the volume of the sample. This volume could be determined within 0.2 cc. with a total volume of about 250 cc., thus giving a possible error of about 0.1 per cent in measuring the volume of the liqiud.

The bomb was then rinsed out three times with redistilled water, free from carbon dioxide, into a 500-cc. Erlenmeyer flask. If the hydroxide content was to be determined, the solution was transferred to a 500-cc. volumetric flask and diluted to volume with the purified water. One portion was then pipetted out to be run for hydroxide and sulphate, and the remaining portion run for carbonate and calcium. The size of the samples to be used depended on the approximate amount of the material present. Thus, with a low sulphate content, 250-cc. samples were used for hydroxide and sulphate determinations and with a high sulphate content only 100 cc. were used. If the hydroxide content was not to be determined, all of the sample was run for carbonate and sulphate.

8. *Method of Analysis.*—Since six bombs were run at one time in the constant-temperature boxes, it was found advantageous to run

the six samples through the analytical procedure together. When the solutions were prepared before adding to the bombs, a blank using the same amount of the carbon dioxide-free redistilled water as was used for the bombs was put in a 500-cc. Erlenmeyer flask, and the same solution added as was added to one of the bombs. The flask was stoppered and set aside to be run through the analytical procedure with the samples obtained from the bombs after they had been held at the desired temperature for the proper period of time. This blank served to check the initial concentration of the solution in the bomb, as well as the analytical procedure.

The solids added to the bombs were either calcium sulphate or calcium carbonate. The calcium sulphate was added in previous tests both as $CaSO_4$ and $CaSO_4 \cdot 2H_2O$, and the resulting solubilities were found to be identical, apparently irrespective of which form was used. For the tests being reported, $CaSO_4$ was added as the solid. When calcium carbonate was added, ground crystals of Iceland spar were used; the latter was of standardization quality.

The chemicals to be added in solution were in about 0.1 molal solutions made by adding them to carbon dioxide-free redistilled water. The sodium hydroxide solution was stored in a paraffin-lined bottle.

The water was obtained by redistillation after adding a small amount of sulphuric acid and potassium permanganate to distilled water and collecting the middle 60 per cent of the distillate. The redistilled water was washed free from carbon dioxide by bubbling carbon dioxide-free air through it for 24 hours. Tests run on liter samples of this water showed the carbon dioxide to be not more than 2 parts per million.

(a) Hydroxide Determination

The hydroxide was determined by pipetting a sample of the solution into a 500-cc. Erlenmeyer flask, 25 cc. of a standard solution of 0.02 *N** sodium hydroxide containing about 10 per cent barium chloride being added; after the mixture had been allowed to stand stoppered for about 2 hours, the solution was titrated with 0.02 *N* hydrochloric acid to the phenolphthalein end point (colorless). A blank was run using the same volume of carbon dioxide-free water as that contained in the sample being tested. The difference between the quantity of acid used for the blank and that used for the sample

*The expression *N* is an abbreviation for normal and corresponds to one gram equivalent weight per liter. Thus a 1 *N* solution of NaOH would be 40 grams per liter and 0.02 *N* solution of NaOH would be 0.02 x 40 or 0.8 grams per liter.

gave a direct measure of the hydroxide content. Tests conducted by the author to check the accuracy of this method* for the determination of hydroxide showed that the possible error was about 3 p.p.m. as sodium hydroxide.

(b) Carbonate Determination

The sample to be tested was transferred to a 1000-cc. Erlenmeyer flask, previously swept clean with carbon dioxide-free air. The flask was connected with a reflux condenser. A stream of carbon dioxide-free air was passed through the flask, through the condenser, through granulated zinc, through calcium chloride, and finally through anhydrone. The dry air was then passed through a weighed Wesson bulb containing ascarite and anhydrone. The entire train was swept free from carbon dioxide before adding the flask containing the sample. After the flask was added, dilute hydrochloride acid (1:1) was added by means of a funnel put through the rubber stopper; the solution was heated to boiling and boiled slowly, air being passed through slowly. After about 30 minutes the Wesson bulb was removed and weighed, the difference in weight being a measure of the carbon dioxide evolved from the solution. Weighed amounts of pure sodium carbonate were put in solution in carbon dioxide-free water, and the carbon dioxide content tested by this method. It was found that the method was accurate to within one p.p.m. of carbon dioxide (0.02 millimole per liter) when a 250-cc. sample was used.

(c) Sulphate Determination

The solution left after the hydroxide determination was made distinctly acid to methyl orange by adding a few drops of concentrated hydrochloric acid. It was then boiled down to about 75 cc. volume, allowed to stand for 12 hours, filtered, washed, ignited, and weighed in tared crucibles as barium sulphate. It was thought that, since the barium sulphate was precipitated by the addition of an alkaline barium chloride solution in the cold, the precipitate might occlude other materials. However, tests run by this method, using standard solutions of sodium sulphate, gave results for the sulphate content within 2 p.p.m. of sulphate (0.02 millimole per liter) of those obtained in a volume of 250 cc. in which the barium sulphate was precipitated from a hot, slightly acid solution.

(d) Calcium Determination

The calcium was determined after the carbonate content determination. The acid solution left after the carbon dioxide had been

*Straub, F. G., Anal. Ed., Industrial and Engineering Chemistry *4*, 290, July 15, 1932.

removed was boiled down to 75 cc., made slightly alkaline with ammonium hydroxide, and then just acid to methyl orange indicator with hydrochloric acid. About 20 cc. of a 4-per-cent solution of ammonium oxalate were added to the boiling solution; after a few minutes of boiling, the solution was made slightly alkaline with ammonium hydroxide and boiled for 15 minutes. After cooling, the solution was made distinctly alkaline with ammonium hydroxide, allowed to stand 12 hours, filtered, and washed with distilled water, slightly alkaline with ammonium hydroxide, until free from ammonium oxalate. The precipitate was dissolved in hot sulphuric acid solution (about 25 cc. concentrated sulphuric acid to 1 liter of water), heated to 176 deg. F., and titrated with 0.05 *N* potassium permanganate solution. The potassium permanganate solution was standardized at regular intervals against sodium oxalate obtained from the Bureau of Standards. If much iron was present, it was removed as ferric hydroxide prior to determining the calcium. When the volume of ferric hydroxide was appreciable, it was dissolved in hydrochloric acid and reprecipitated, and the filtrate added to the first filtrate and run for calcium. The calcium was determined with an error of $\pm$ 0.2 milligram. Thus, on a 250-cc. sample the error would be $\pm$ 0.02 millimole per liter.

In order to find the degree of accuracy with which the calcium and sulphate could be determined, solutions of calcium sulphate were made, using pure $CaSO_4 \cdot 2H_2O$ and redistilled water. The solid calcium sulphate used was analyzed by an independent analyst who determined the calcium as calcium oxalate, igniting to the oxide and weighing. The sulphate was determined as barium sulphate. The results of his duplicate analyses in per cent composition were as follows:

	Sample 1	Sample 2	Average	Water Free Basis	Theoretical Composition
CaO	31.90	31.69	31.79	41.6	41.3
SO_3	44.94	44.94	44.94	58.8	58.7
Ignition loss	23.67	23.67	23.67	0.0	0.0

A solution was made from a weighed amount of this salt calculated to have 200 p.p.m. of $CaSO_4$. Samples of various amounts were taken for analysis for calcium and sulphate. The results of these tests are given in Table 1.

This shows that the calcium could be determined within an error of about $\pm$ 0.2 milligram, and the sulphate within about the same error. Thus, if a solution from the bombs containing about 1 millimole per liter of calcium sulphate were analyzed, there would be approximately 40 p.p.m. calcium and 96 p.p.m. sulphate. With a 250-cc.

TABLE 1

RESULTS OF ANALYSES OF STANDARD SOLUTIONS OF CALCIUM SULPHATE

Volume of Solution Used cc.	$KMnO_4$ Used cc.	Amount of Ca			Weight of $BaSO_4$ gram	Amount of SO_4		
		Detd. from titration gram	Theoretical gram	Difference* gram		Detd. from $BaSO_4$ gram	Theoretical gram	Difference* gram
50	3.00	0.0031	0.0029	+0.0002	0.0176	0.0072	0.0071	+0.0001
100	5.80	0.0059	0.0058	+0.0001	0.0336	0.0138	0.0141	−0.0003
250	14.45	0.0147	0.0145	+0.0002	0.0858	0.0352	0.0353	−0.0001

*Determined minus theoretical.

TABLE 2

SOLUBILITY OF CALCIUM SULPHATE

Temperature deg. F.	Ca	SO_4	Temperature deg. F.	Ca	SO_4
	millimoles per liter			millimoles per liter	
360	0.85	0.93	470	0.37	0.17
	0.85	0.85		0.30	0.19
	0.91	0.71		0.30	0.19
	0.87	0.75		0.38	0.22
	0.81	0.77		0.36	0.25
	0.96	0.75		0.34	0.20
	0.92	0.85			
	1.02	0.85			
Average	0.90	0.81	Average	0.34	0.20
405	0.51	0.45	600	0.20	0.09
	0.52	0.50		0.26	0.10
	0.49	0.44		0.25	0.10
	0.48	0.43		0.19	0.05
	0.58	0.32		0.21	0.10
	0.52	0.45		0.27	0.05
	0.56	0.48			
Average	0.52	0.44	Average	0.23	0.08

sample to analyze, and using 125 cc. for each, there would be 5 milligrams of calcium and 12 milligrams of sulphate. With an error of about ± 0.2 milligram in analysis, the resultant analyses should agree within + 0.04 millimoles per liter for both calcium and sulphate. This error would be about the same for all solutions until the concentrations became lower than 0.2 millimole per liter, when it might become somewhat greater.

9. *Test Data from Solubility Tests.*—The data obtained from the tests are given in Tables 2 to 11 inclusive.

Table 2 gives the results of the solubility tests using calcium sulphate as a solid phase. It is to be noted that the sulphate is consist-

ently lower than the calcium. This is not an experimental error, since the analyses of samples of calcium sulphate solutions, made at room temperatures to similar concentrations, checked within 0.04 millimole per liter. The higher calcium value may be explained on the basis that a small amount of $Fe(OH)(SO_4)$ may have formed owing to the reaction within the bomb at the high temperatures. With this in the solid phase, there would be a tendency to have a low sulphate content in the liquid phase. This appeared to be possible, since the remaining solid phase always had a reddish color and appeared to be coated with a thin red film of some iron compound. If the 400 cc. of solution in contact with the solid phase were low (about 0.10 millimole per liter of sulphate), this would correspond to about 0.0038 gram of sulphate retained in the solid phase. Since about 4 grams of calcium sulphate were used in the solid phase, and since it is almost impossible to remove the salt which adheres to the inside walls of the bombs, analysis of the solid phase at the end gave no check on the real composition of the solid phase.

In order to be certain that there was not a slight excess of calcium in the calcium sulphate, such as calcium carbonate or hydroxide, the salt was digested with hydrochloric acid and washed thoroughly with redistilled water. When this washed calcium sulphate was used as the solid phase the results were the same as before. Calcium sulphate made by different manufacturers gave the same results. All of this indicates that there is undoubtedly a reaction involving the iron from the containers. In order to study the effect of iron, a powdered iron was added with the calcium sulphate as a solid phase. The presence of large excesses of the iron had no apparent effect on the resulting calcium and sulphate contents. This apparently indicated that a hydrolysis of a small amount of the calcium sulphate took place, and that the sulphate combined with the iron to form the hydroxide of ferric sulphate; apparently this was adsorbed on the solid phase, reducing the sulphate content a small amount. The solutions taken from the solubility tests of the calcium sulphate in water had a pH value of approximately 8.0, which also would indicate hydrolysis of the calcium sulphate. However, since the solubility data being collected were to be correlated with data obtained in boiler operation where similar reactions might take place, no attempt was made to run tests in containers free from iron.

Table 3 gives the results of tests having a solid phase of calcium sulphate to which sodium sulphate has been added. These results show how the introduction of a small amount of sodium sulphate

TABLE 3

SOLUBILITY OF CALCIUM SULPHATE IN PRESENCE OF SODIUM SULPHATE

Temperature deg. F.	Ca	SO_4		Temperature deg. F.	Ca	SO_4	
		at end of test	added			at end of test	added
	millimoles per liter				millimoles per liter		
360.....	0.78	0.81	0.25	470.....	0.25	0.27	0.25
	0.69	0.87	0.25		0.24	0.56	0.50
	0.66	0.90	0.50		0.22	1.35	1.25
	0.53	1.49	1.25		0.15	3.28	3.55
	0.54	1.38	1.25		0.17	12.0	11.85
	0.46	3.38	3.55		0.20	13.1	11.85
	0.45	11.90	11.85		0.20	17.8	17.80
	0.49	11.70	11.85				
	0.42	17.50	17.80				
	0.50	17.90	17.80				
405.....	0.41	0.41	0.50	600.....	0.08	0.33	0.25
	0.28	2.74	3.55		0.11	0.94	1.25
	0.28	3.10	3.55		0.04	1.07	1.25
	0.32	11.20	11.85		0.02	3.45	3.55
	0.29	11.30	11.85		0.06	20.4	20.30
	0.29	17.5	17.80				

TABLE 4

SOLUBILITY OF CALCIUM SULPHATE IN PRESENCE OF SODIUM HYDROXIDE

Temperature deg. F.	Ca	SO_4	NaOH		Temperature deg. F.	Ca	SO_4	NaOH	
			at end of test	added				at end of test	added
	millimoles per liter					millimoles per liter			
360.....	0.78	2.00	7.0	12.0	540.....	0.18	1.57	5.4	12.0
	0.73	7.00	23.8	40.0		0.15	6.05	21.6	40.0
	0.77	12.50	32.2	60.0		0.07	11.80	31.2	60.0
470.....	0.14	1.53	5.0	12.0	600.....	0.02	0.71	0.7	12.9
	0.13	6.30	22.8	40.0		0.02	8.10	22.4	43.0
	0.20	11.80	30.5	60.0		0.02	7.15	21.7	43.0
						0.01	14.3	31.1	64.5

(1 millimole per liter) reduces the solubility of the calcium, and that larger amounts of the sulphate have but a small additional influence on the solubility of the calcium.

Table 4 gives the results of tests having a solid phase of calcium sulphate to which sodium hydroxide has been added. The hydroxide content apparently does not influence the solubility of the calcium at 360 deg. F., but at the higher temperatures it reduces it to a marked extent.

TABLE 5

CALCIUM, SULPHATE, AND CARBONATE CONTENT OF SOLUTIONS OF SODIUM CARBONATE HEATED IN CONTACT WITH SOLID CALCIUM SULPHATE

Temperature deg. F.	Ca	Na_2CO_3 added	SO_4 at end of test	CO_3 at end of test	Ratio CO_3 to SO_4	
	millimoles per liter				millimoles	p.p.m.
360	0.81	0.48	1.07	0.39	0.36	0.22
	0.47	1.20	1.63	0.51	0.31	0.19
	0.46	1.20	1.56	0.55	0.35	0.22
	0.44	3.60	3.28	0.73	0.22	0.14
	0.45	12.00	11.50	1.12	0.09	0.06
	0.39	18.00	16.80	1.21	0.07	0.05
405	0.44	0.24	0.43	0.52	1.21	0.79
	0.47	0.48	0.50	0.67	1.34	0.84
	0.34	1.20	1.20	0.75	0.62	0.39
	0.28	3.60	3.25	0.90	0.27	0.17
	0.21	12.00	11.90	1.05	0.09	0.06
	0.23	18.00	17.05	1.40	0.08	0.05
470	0.31	0.48	0.23	0.34	1.47	0.92
	0.24	1.20	0.71	0.90	1.27	0.79
	0.14	3.60	2.78	1.63	0.59	0.37
	0.18	12.00	10.40	2.33	0.22	0.14
	0.17	18.00	15.40	3.73	0.24	0.15
540	0.14	3.60	2.62	1.61	0.62	0.39
	0.08	12.00	10.75	3.83	0.35	0.22
	0.09	18.00	16.00	3.60	0.22	0.14

The results of the tests given in Table 5 are extremely interesting. In the tests reported there calcium sulphate in excess was in contact with a solution of sodium carbonate at the beginning. This involves a study of the reaction

$$CaSO_4 + Na_2CO_3 \leftrightarrows CaCO_3 + Na_2SO_4$$

starting from the left and proceeding to the right. These data show the carbonate content at the beginning, and the carbonate and sulphate content when apparent equilibrium has been reached. The ratio of carbonate to sulphate is also calculated both on the basis of millimoles per liter and parts per million. This ratio does not reach a constant value, but is continually decreasing as the concentration of sulphate increases.

The results of the tests run using solid calcium sulphate and a solution containing sodium chloride, sodium hydroxide, and sodium carbonate are given in Table 6. The sodium chloride was 2.5 millimoles per liter, and the sodium hydroxide 11.5 millimoles per liter at the beginning of all tests. These results are very interesting in that they show that the carbonate remains almost constant at all concentrations and at all temperatures, with the exception of 540 deg. F.,

TABLE 6

SULPHATE, CARBONATE, AND HYDROXIDE CONTENT OF SOLUTIONS CONTAINING SODIUM CARBONATE, HYDROXIDE, AND CHLORIDE, HEATED IN CONTACT WITH SOLID CALCIUM SULPHATE

(NaCl added, 2.5 millimoles per liter in all tests; NaOH added, 11.5 millimoles per liter in all tests)

Temperature deg. F.	Na_2CO_3 added	SO_4 at end of test	CO_3 at end of test	OH at end of test	Ratio CO_3 to SO_4	
	millimoles per liter				millimoles	p.p.m.
360	0.44	1.93	0.29	4.7	0.15	0.09
	0.44	1.71	0.43	5.9	0.25	0.16
	0.68	1.77	0.41	5.2	0.23	0.14
	0.68	2.25	0.44	4.5	0.19	0.12
	1.40	2.82	0.37	4.0	0.13	0.08
	3.80	4.88	0.33	3.2	0.068	0.04
	3.80	4.68	0.27	3.1	0.058	0.04
	12.00	11.70	0.40	3.9	0.034	0.02
	12.00	12.78	0.46	3.6	0.036	0.02
	18.00	22.40	0.78	2.6	0.035	0.02
405	0.44	1.45	0.42	5.3	0.29	0.18
	0.68	1.92	0.28	6.0	0.15	0.09
	1.40	2.80	0.59	5.5	0.21	0.13
	3.80	4.60	0.54	4.6	0.12	0.08
	12.00	12.30	0.41	2.8	0.033	0.02
	12.00	12.62	0.73	5.3	0.057	0.04
	18.00	18.05	0.54	2.9	0.030	0.02
470	0.44	1.35	0.31	3.3	0.23	0.15
	0.68	1.71	0.41	3.5	0.24	0.15
	1.40	2.50	0.94	4.0	0.38	0.24
	1.40	2.61	0.40	3.0	0.15	0.09
	3.60	4.44	1.05	2.1	0.24	0.15
	12.00	12.72	0.47	2.8	0.037	0.02
	12.00	12.82	0.66	2.7	0.051	0.03
	18.00	19.85	0.85	3.7	0.043	0.02
540	0.44	0.85	0.22	3.2	0.26	0.16
	0.44	0.88	0.46	4.0	0.52	0.32
	0.68	1.47	0.37	2.8	0.25	0.16
	1.40	2.20	0.27	2.6	0.12	0.08
	1.40	2.51	0.61	3.5	0.24	0.15
	3.80	4.83	0.57	2.8	0.12	0.08
	12.00	12.75	0.66	2.5	0.05	0.03
	18.00	19.30	3.78	4.0	0.19	0.12
	18.00	18.15	2.33	3.5	0.12	0.08

where it increases in the last two tests reported. This may be due to the coating of the calcium sulphate with calcium carbonate, where an excess of sodium carbonate was obtained. The remaining hydroxide varies to some extent and may be influenced by the variation in the amount of solid at the beginning, since this was not constant. The almost constant value of the reported carbonate is undoubtedly due to the fact that in the presence of sodium hydroxide another equilibrium is established which is apparently independent of the one under consideration. Thus, if sodium carbonate is present in solution at these temperatures and the corresponding steam pressures, the following reaction may take place:

$$2Na_2CO_3 + 2H_2O \leftrightarrows NaHCO_3 + 3NaOH + CO_2$$

TABLE 7

SOLUBILITY OF CALCIUM CARBONATE

Temperature deg. F.	Ca millimole per liter	Temperature deg. F.	Ca millimole per liter	Temperature deg. F.	Ca millimole per liter	Temperature deg. F.	Ca millimole per liter
360.....	0.25	405.....	0.17	470.....	0.13	600.....	0.07
	0.26		0.14		0.13		0.09
	0.20		0.14		0.11		0.06
	0.25		0.11		0.13		0.07
	0.29		0.13		0.09		0.09
	0.27		0.16		0.10		0.11
Average..	0.25	Average.	0.14	Average.	0.11	Average.	0.08

When a sample of the solution is analyzed at room temperature the carbonate is reported, whereas it undoubtedly existed as acid carbonate at the elevated temperature. The acid carbonate present at these higher temperatures would depend upon the partial pressure of the carbon dioxide and the hydroxide concentration. The carbonate being present as acid carbonate, no reaction would take place between it and the calcium sulphate. Under these conditions the reported carbonate, having been acid carbonate at the higher temperatures, would remain constant and be almost independent of the sulphate concentration.

Table 7 gives the solubility of calcium carbonate. The partial pressure of the carbon dioxide was not controlled, but was that corresponding to the equilibrium at the various temperatures. This was found to be 0.00015 atm. at 360 deg. F. Any change in the partial pressure of the carbon dioxide would undoubtedly affect the solubility of the calcium.

The solubility of calcium carbonate decreases as the temperature increases. This is in accord with the work of Frear and Johnston.* The results obtained are somewhat higher than the values calculated by Partridge.†

Tests were run in which sodium carbonate was added to the liquid phase with calcium carbonate as the solid phase. The results of these tests were extremely interesting since the calcium dropped to less than 0.5 p.p.m. (0.01 millimole per liter) when 0.25 millimoles per liter of sodium carbonate was added and remained as low as this even when the sodium carbonate content was as high as 18 millimoles per liter.

*Frear and Johnston, Jour. Am. Chem. Soc. *51*, 2082 (1929).
†Engineering Research Bulletin No. 15, University of Michigan, 1930.

TABLE 8

CALCIUM, CARBONATE, AND HYDROXIDE CONTENT OF SOLUTIONS CONTAINING SODIUM HYDROXIDE HEATED IN CONTACT WITH SOLID CALCIUM CARBONATE

(CO_3 in solution without any solid phase, 0.20 millimole per liter)

Temperature deg. F.	NaOH added	Ca at end of test	CO_3 at end of test	NaOH at end of test
	millimoles per liter			
360	11.5	0.0	0.86	5.1
	11.5	0.0	1.18	6.6
	11.5	0.0	0.94	5.7
	11.5	0.0	1.49	5.9
	11.5	0.0	1.00	6.3
	11.5	0.0	1.15	5.0
	11.5	0.0	0.17	5.4

Tests run at 405, 470 and 540 deg. F. all showed the Ca to be zero at the end.

TABLE 9

SOLUBILITY OF CALCIUM CARBONATE IN PRESENCE OF SODIUM SULPHATE

Temperature deg. F.	Ca	SO_4	Temperature deg. F.	Ca	SO_4
	millimoles per liter			millimoles per liter	
360	0.25	0.00	470	0.11	0.00
	0.27	3.58		0.08	3.17
	0.32	11.85		0.11	11.5
	0.47	17.8		0.14	16.4
	0.44	17.8			
405	0.14	0.00	600	0.08	0.00
	0.17	1.18		0.07	3.00
	0.29	3.58		0.02	2.65
	0.25	11.85		0.02	11.60
	0.32	17.8		0.02	19.40
	0.29	17.8			

When the calcium carbonate was heated in contact with sodium hydroxide, the calcium content was also found to be zero, as shown in Table 8.

Table 9 gives the results of tests using a solid phase of calcium carbonate and adding sodium sulphate to the liquid phase. It is interesting to note that at 360 and 405 deg. F., as the sulphate increases, the calcium increases, so that in the solutions of higher sulphate content the calcium content is equal to that found when calcium sulphate was the solid phase and the sodium sulphate content was high.

Table 10 gives the results of adding a solution of sodium sulphate, hydroxide, and chloride to solid calcium carbonate. It shows clearly

TABLE 10

SULPHATE, CARBONATE, AND HYDROXIDE CONTENT OF SOLUTIONS CONTAINING SODIUM SULPHATE, HYDROXIDE, AND CHLORIDE HEATED IN CONTACT WITH SOLID CALCIUM CARBONATE

(NaCl, 2.5 millimoles per liter in all tests; NaOH, 11.5 millimoles per liter in all tests)

Temperature deg. F.	SO_4 added	SO_4 at end of test	CO_3 at end of test	OH at end of test	Ratio CO_3 to SO_4	
	millimoles per liter				millimoles	p.p.m.
360	0.25	0.32	0.62	6.6	1.94	1.21
	0.50	0.48	0.66	5.1	1.37	0.85
	0.50	0.48	0.96	6.0	2.00	1.25
	1.25	1.32	1.08	5.5	0.82	0.51
	1.25	1.28	1.09	6.5	0.85	0.53
	3.75	3.96	1.19	4.8	0.30	0.19
	3.75	3.86	1.00	6.5	0.26	0.16
	12.50	8.95	1.27	7.0	0.14	0.09
	18.75	18.8	1.28	5.8	0.068	0.04
405	0.25	0.12	0.20	5.9	1.67	1.04
	0.25	0.13	0.26	6.5	2.00	1.25
	0.50	0.16	0.18	4.9	1.12	0.70
	1.25	0.18	0.61	6.2	3.38	2.10
	1.25	1.40	1.09	5.8	0.78	0.49
	3.75	3.70	0.70	6.0	0.19	0.12
	12.50	13.0	0.70	5.0	0.054	0.03
	18.75	18.65	1.21	6.5	0.065	0.04
470	0.25	0.12	0.55	5.7	4.58	2.86
	0.25	0.15	0.41	6.5	2.74	1.71
	0.50	0.18	0.32	7.2	1.78	1.11
	1.25	1.85	1.58	4.8	0.85	0.53
	3.75	4.75	0.94	5.5	0.20	0.12
	12.50	13.5	0.38	6.3	0.028	0.02
	18.75	19.4	2.24	6.0	0.12	0.08
540	0.25	0.09	0.86	4.5	9.55	5.95
	0.25	0.11	0.82	4.0	7.45	4.65
	0.50	0.13	0.70	3.7	5.40	3.36
	1.25	1.96	1.93	1.1	0.98	0.61
	3.75	2.81	1.12	2.5	0.40	0.25
	12.50	13.8	2.30	2.8	0.16	0.10
	18.75	21.4	2.78	3.2	0.13	0.08
	18.75	19.6	1.33	2.5	0.068	0.04

that the sulphate added remained in solution and no calcium sulphate was precipitated or formed.

Table 11 gives the amounts of calcium and sulphate in solution when solid calcium sulphate and calcium carbonate is in contact with distilled water. Additional tests were run using calcium carbonate and calcium sulphate as a solid phase and adding sodium carbonate, sodium sulphate, sodium hydroxide, sodium hydroxide and sodium carbonate, and sodium hydroxide plus sodium sulphate. The results obtained were almost identical with those reported when calcium sulphate alone was used. Consequently they are not given here in detail.

10. *Discussion of Results of Solubility Tests.*—The results of these tests should serve to give a thorough understanding of which phase is

TABLE 11

SOLUBILITY OF CALCIUM SULPHATE AND CALCIUM CARBONATE COMBINED

Temperature deg. F.	Ca	SO_4	Temperature deg. F.	Ca	SO_4
	millimoles per liter			millimoles per liter	
360	0.88	0.78	470	0.29	0.18
	0.83	0.70		0.29	0.15
	0.84	0.76		0.30	0.22
	0.83	0.77		0.29	0.20
	0.79	0.76			
Average	0.85	0.75	Average	0.29	0.19
405	0.53	0.41	540	0.16	0.11
	0.51	0.43		0.12	0.15
	0.41	0.47		0.22	0.07
	0.49	0.35		0.18	0.15
Average	0.49	0.41	Average	0.17	0.12

stable in contact with solutions having various ions in solution. Thus, when solid calcium carbonate is in contact with a solution of sodium hydroxide the solubility of calcium is not more than 0.01 millimoles per liter, as shown in Table 8. The sodium hydroxide might react with the calcium carbonate to form calcium hydroxide and sodium bicarbonate. The sodium bicarbonate would be controlled by the partial pressure of the carbon dioxide. The results obtained in Table 8 indicate that this is possible. The calcium solubility is 0.0 millimole; the hydroxide concentration has been reduced; and the carbonate varies to a large extent. The addition of sodium sulphate to this system should have no influence on the carbonate content if no calcium sulphate existed or was formed as a solid phase. However, if calcium sulphate were formed, then the carbonate should drop to the lower value reported in Table 6.* The fact that the sulphate remaining at the end is the same as that added, except in the very low concentrations, where occlusion of the sodium sulphate by the calcium carbonate, or reaction with the iron container, would readily explain the small losses, would indicate that no calcium sulphate existed as a solid. Under these conditions the results reported in Table 10 should not check those in Table 6. The solids in the tests reported in Table 10 were undoubtedly basic calcium carbonate as well as calcium hydroxide. If calcium hydroxide alone had been formed, there would have been a much larger increase in carbonate content. This indicates that a basic calcium carbonate was undoubtedly formed.

*The results given in Tables 21 and 22 show that the presence of sodium chloride does not influence this reaction to an appreciable extent.

In order to predict the concentration of the carbonate ion necessary to cause preferential precipitation of calcium carbonate, it would be necessary to determine the relative solubility of the calcium carbonate and calcium sulphate in the presence of the various ions and in solutions of ionic strengths similar to those encountered. Thus in the presence of sodium hydroxide the solubility of calcium carbonate is not more than 0.01 millimole, while the solubility of calcium sulphate is 0.90 millimole at 360 deg. F. and 0.23 millimole at 600 deg. F. Under these conditions the presence of a ratio of carbonate to sulphate at the temperatures under consideration greater than approximately 0.01 should cause precipitation of the carbonate in preference to the sulphate.

If a solution of sodium hydroxide is added to solid calcium carbonate and heated to the temperatures under consideration, the ratio of carbonate to sulphate will be infinite, since the sulphate is zero. There will be some acid carbonate in solution, and the equilibrium will be

$$CaCO_3 + 2NaOH \leftrightarrows Na_2CO_3 + Ca(OH)_2$$

If sodium sulphate is added in sufficient amount to make the ratio of carbonate to sulphate less than 0.01, calcium sulphate should precipitate. The carbonate content is high because of the reaction between the sodium hydroxide and the calcium carbonate. Before the ratio of carbonate to sulphate becomes less than 0.01, it is necessary to have the sulphate at least 30 millimoles per liter (or 5200 p.p.m. sodium sulphate), which is much higher than the sulphate content of the tests reported, and this explains why no calcium sulphate was formed in the tests reported in Table 10.

The results in Table 6 show that the reported carbonate is independent of the sulphate concentration up to at least 22 millimoles per liter of sulphate. Thus, if solid calcium sulphate is in contact with a solution containing sodium hydroxide, the introduction of sodium carbonate into the solution forms carbonate ions which, because of the low sulphate content from the calcium sulphate solubility, give a carbonate concentration sufficient to precipitate calcium carbonate, which reduces the carbonate. As long as solid calcium sulphate exists, the sodium carbonate added will react to precipitate calcium carbonate and form soluble sodium sulphate until the sulphate concentration becomes high enough to require an appreciable carbonate increase. However, this concentration is higher than 22 millimoles of sulphate (about 3000 p.p.m. sodium sulphate). Since the carbonate

reported is the total of the acid carbonate and carbonate existing at the higher temperature, and since there is no marked increase in the reported carbonate even with the sulphate equal to 22 millimoles per liter, the carbonate existing at the higher temperatures must be low in respect to the acid carbonate.

The data reported in Tables 6, 7, and 10 indicate that, in order to maintain a stable phase of calcium carbonate, only a small amount of sodium carbonate is necessary. Thus, with the sulphate as high as 22.40 millimoles per liter (2150 p.p.m. SO_4), a carbonate content as low as 0.78 millimole per liter (47 p.p.m. CO_3) should prevent the formation of calcium sulphate.

The solubility of calcium carbonate, in the presence of sodium hydroxide, being zero for all practical cases, gives further insight into the question of scale formation and prevention in steam boilers. Carbonate scale forms readily in feedwater heaters and hot water lines, owing to the partial breakdown of the calcium bicarbonate to form the less soluble calcium carbonate. Such precipitation takes place rapidly and the precipitate forms on the areas being heated, as well as on the cooler portions. However, with the calcium bicarbonate entering the boiler, which contains free hydroxide in the majority of instances, the solubility is reduced to zero, and the solid phase forms evenly throughout the boiler irrespective of the temperatures. If at any time the hydroxide and carbonate alkalinity disappear and the sulphate content increases, then sulphate scale is formed. The solubility of the calcium sulphate is appreciable. Consequently, it is deposited at the heating surface. Small amounts of sodium carbonate in the presence of hydroxide are sufficient to prevent formation of the solid-phase calcium sulphate, even at a temperature as high as 540 deg. F.

A feed water which contains a small amount of sodium carbonate in excess of the theoretical amount required to react with the calcium sulphate present will form sodium hydroxide in the boiler. However, in the average boiler not over 90 per cent of the sodium carbonate decomposes to form sodium hydroxide, and 10 per cent remains in the boiler. Thus, if the total alkalinity (expressed as sodium carbonate) of a boiler water becomes 500 p.p.m., there will be 50 p.p.m. of sodium carbonate remaining in the boiler (when analyzed at room temperature), or approximately 0.5 millimole of carbonate, and calcium sulphate scale should be prevented even if the boiler was operating at 1000 pounds steam pressure.

The direct interpretation of these solubility data in terms of boiler operation should be made conservatively. These are equilibrium data, and, until they are correlated with data from actual boiler operation, no specific conclusions should be drawn. There is a possibility that the rate of steam generation at the heating surface may have more to do with the rate of scale formation than the question of solubility, and, furthermore, it is possible that the equilibrium conditions may not be maintained in the various portions of an operating boiler.

In view of these facts, the investigation reported in Chapters IV and V was conducted.

11. *Conclusions.*—The conclusions which may be drawn are as follows:

(1) The solubility of calcium carbonate decreases with increase in temperature.

(2) The solubility of calcium carbonate in the presence of sodium carbonate or hydrate is practically zero at the temperatures studied.

(3) The solubility of calcium sulphate is not directly proportional to the sulphate in solution.

(4) Calcium sulphate as a solid phase cannot exist in equilibrium with solutions containing over 30 parts per million of sodium carbonate, even at a pressure of 1000 lb. per sq. in.

(5) The old calculated ratios of CO_3/SO_4 to prevent calcium sulphate formation as a solid phase are extremely high.

III. Decomposition of Sodium Carbonate Solutions in Boiler Waters

By R. F. Larson*

12. *Object of Laboratory Tests.*—The carbonates of sodium are very soluble and often are found in large quantities in both natural and treated waters. In natural waters the bicarbonate form is usual, due to the presence of more than enough carbon dioxide in solution to maintain the carbonate. The excess carbon dioxide is, however, loosely held, and is driven off on being heated, the reaction being practically complete at 212 deg. F. The carbonate formed and remaining resists further decomposition at these temperatures. However, in 1891 Paul† observed the development of a distinct causticity

*Instructor in Mechanical Engineering.
†Paul, J. H., Trans. Soc. Engrs. 147-86 (1891).

or sodium hydroxide alkalinity in the water of a steam boiler, using as a feed water a natural water containing sodium bicarbonate.

Many others have since observed and studied the phenomenon. The presence of carbon dioxide in the steam space and headers in amount in excess of that accounted for as free or loosely held carbon dioxide in the feedwater, led several to suspect that this and the accompanying causticity resulted from the final break-down of the normal carbonate.

Paul in 1919* proposed that the principal decomposition reaction was not toward the liberation of carbon dioxide in the steam, but rather toward that of oxygen. He apparently found much evidence of oxygen in the condensed steam and little carbon dioxide, and therefore proposed the following:

$$Na_2CO_3 + H_2O \rightarrow HCO_2Na + NaOH + 1/2\,O_2 \qquad (1)$$

The formate of soda then went through a complicated series of reactions forming various organic compounds, some being reconverted with caustic soda back to sodium carbonate.

Hall, Kartch, and Robb,† in 1927, conducted an investigation of the noncondensable gases in the steam from a small laboratory boiler. When sodium carbonate was introduced with the feed, carbon dioxide constituted most of the noncondensable gas in the steam taken off. The oxygen content was exceedingly small and did not increase when sodium carbonate was introduced. In fact, they found no evidence for the existence of reaction (1), and concluded that the principal reaction was probably

$$Na_2CO_3 + 2H_2O \rightarrow 2NaOH + H_2O + CO_2 \qquad (2)$$

The caustic alkalinity of the boiler water was observed to increase steadily as the boiler was heated, samples of steam and of water being drawn off for analysis. Other investigators have also shown that the second reaction occurs, and at temperatures below 212 deg. F. is too slow to be measured.

Sodium carbonate is found present in almost all boiler waters. It is the chief ingredient of many boiler compounds. In the lime-soda method of water softening exterior to the boiler, it may be added in excess. The base exchange or zeolite process forms sodium bicarbonate when used on certain types of water. The use of phosphates either

*Paul, J. H., "Boiler Chemistry and Feed Water Supplies," Longman's Green (1919).
†Carnegie Institute of Technology Bulletin 24 (1927).

as a water softener or as an internal treatment in the boiler drum causes it to be formed in certain types of water.

The extent of this decomposition phenomenon in a particular boiler is of importance to the boiler operator in various ways. The presence of sodium hydroxide and the absence of sufficient quantities of certain inhibitors has been established as the chief contributing cause of caustic embrittlement, an intercrystalline cracking of the boiler plate which occurs in the seams and highly stressed areas of the boiler. Parr and Straub* have definitely shown that the concentration of this caustic is possible in the seams and capillary spaces of the boiler, and to an extent sufficient to attack the grain boundaries of the adjacent highly stressed metal. Among the inhibitors are sodium carbonate and sodium sulphate. The presence of the latter in sufficient quantities is known to effectively prevent this type of cracking, and is recommended in the A.S.M.E. Code.† In calculating the quantity of sodium sulphate necessary, the carbonate has been assumed as potential hydroxide, and the ratios (of the sodium sulphate to the total alkalinity) for various pressures are based on total alkalinity. The maintenance of these ratios has put a heavy burden on the boiler-plant operator who is also striving to keep concentration down by means of blowdown. It naturally results in excessive blowdown.

Later developments in the study of embrittlement have shown that the 1 to 1 ratio may be a trifle low, the other ratios amply safe, and that the sodium carbonate present may also act as an inhibitor. Figure 5 is a chart taken from Bulletin No. 216 of the University of Illinois Engineering Experiment Station, "Embrittlement in Boilers," by F. G. Straub. It is drawn from data on the solubility relations of sodium carbonate and sodium sulphate in a solution of 100 grams per liter of sodium hydroxide, a concentration of caustic found necessary to embrittle specimens in the laboratory. Wherever this concentration could be reached with sodium carbonate and sodium sulphate still in solution, embrittlement has occurred; wherever the ratios were such that these salts would precipitate out before this dangerous concentration was reached in the boiler seams, boilers were not embrittled. This chart shows clearly the extent to which carbonate is an inhibitor, and explains why certain boilers have operated for years with a high carbonate content in the boiler and with little sulphate without experiencing embrittlement. It offers the plant operator a chance to

*Bulletins 155, 177, and 216 of the Engineering Experiment Station, University of Illinois.
†A.S.M.E. Boiler Construction Code, 1932.

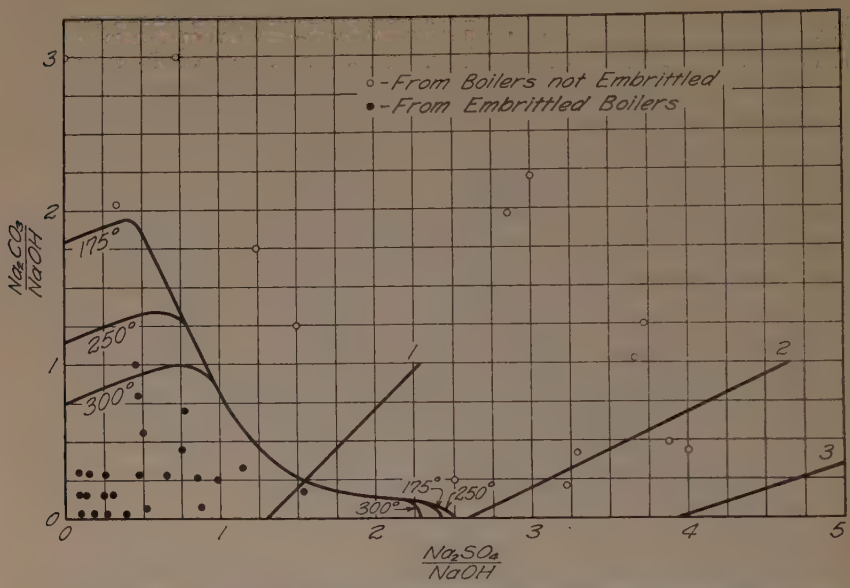

FIG. 5. RATIOS OF $Na_2CO_3/NaOH$ AND $Na_2SO_4/NaOH$ NECESSARY TO PREVENT EMBRITTLEMENT

use the inhibiting power of carbonate in calculating the amount of sulphate necessary to insure safety from this type of cracking.

The presence of hydroxyl alkalinity to a limited extent has been shown to inhibit corrosion. The maintenance of a hydroxyl-ion concentration of about 100 parts per million and a pH value of from 9 to 10.5 has been recommended.* Soda ash is often used in small quantities to build up hydroxyl alkalinity and at the same time increase the pH value.

The maintenance of a carbonate-sulphate ratio has been recommended as a preventative for the deposition of a calcium sulphate boiler scale.†

An attempt to obtain this information in a quantitative way from an operating boiler was reported by Joos.‡ An interesting compilation of boiler water data was made from a large number of power boilers operating at various pressures and ratings. Due to the wide variation in this data and the lack of correlation, it was apparent that the reaction would have to be studied in an experimental boiler under controlled conditions. Hall, Kartch and Robb unfortunately

*Hall and Mumford; Heating, Piping and Air Conditioning, Journal Section of A.S.H.V.E., 1931, p. 943.
†Carnegie Institute of Technology Bulletin 24 (1927).
‡Joos, C. E. Power, Nov. 12, 1929, pp. 762-764.

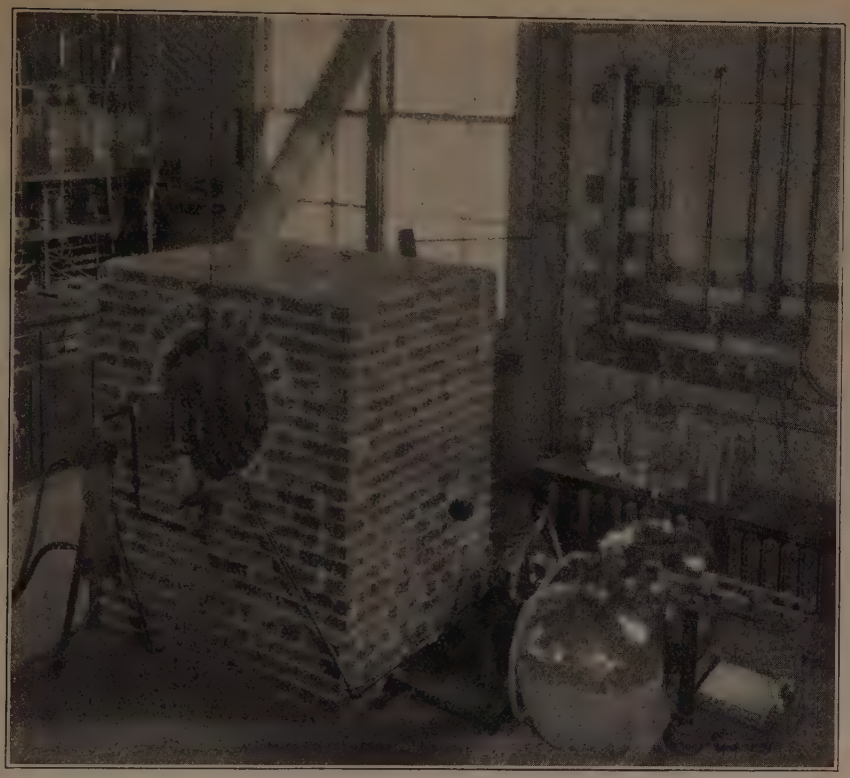

FIG. 6. APPARATUS USED IN TESTS OF DECOMPOSITION REACTION IN VARIOUS SYNTHETIC CARBONATE WATERS

did not duplicate the operations of an industrial boiler in such particulars as continuous feed and constant water level, and consequently their work had little practical application. Furthermore, the operating pressures were not comparable to those found in the modern boiler.

In order to obtain accurate comparable data, the author undertook to build and operate a small high-pressure laboratory boiler, in which all of the operations of an industrial boiler could be duplicated on a controllable scale.

13. *Apparatus for Tests on Laboratory Boiler.*—The apparatus used is pictured in Figs. 6 and 7. It consisted of a 10-in. extra-heavy seamless tube 30 in. long and heavily flanged at the ends so as to make up a cylindrical boiler suitable for high pressures. All connections to the boiler were made through the flanges, as shown in Fig. 7. The boiler was then suspended from a steel frame, and the furnace

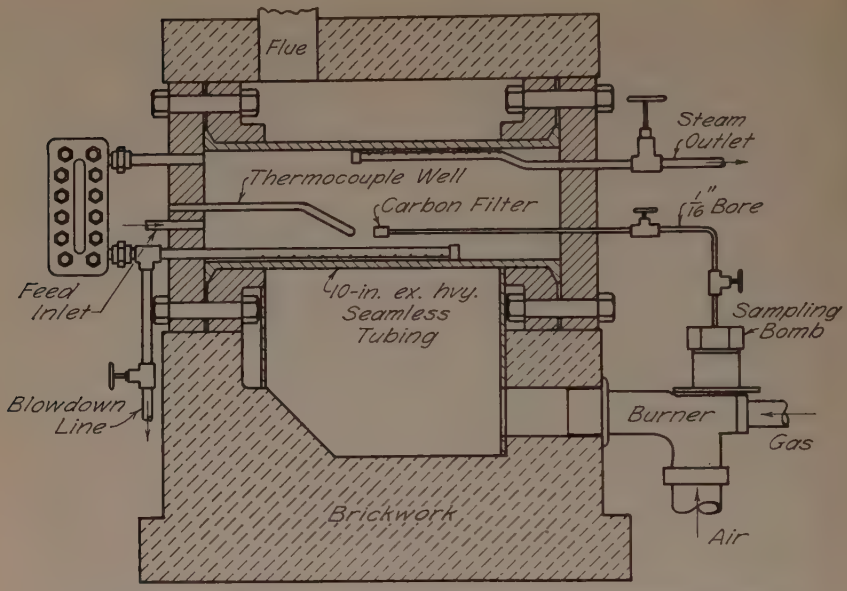

FIG. 7. SECTIONAL VIEW OF BOILER OF TEST APPARATUS SHOWN IN FIG. 6

chamber was bricked in as shown. At a later date Transite baffles were added to protect the studs from the action of excessive heat.

The feedwater inlet was at the left or front end. A special high-pressure gage glass was procured and installed as shown. A blowdown line with valve was installed, as was also a blowdown condenser permitting volumetric measurement of blowdown at room temperature. A steel thermocouple well was installed as shown and bent so as to be completely immersed. An iron-constantan couple was made and inserted, with leads properly insulated with asbestos. A Leeds and Northrup recording potentiometer was used to obtain a temperature check on the reading of a pressure gage installed on the opposite end of the boiler.

In the rear flange was fitted a steam outlet with a needle-valve control. This led to a steam condenser from which condensate could be drawn into 5-gal. bottles and analyzed for alkalinity and carbon dioxide. Samples of boiler water were drawn off through a carbon filter and capillary tube into a steel bomb of about 300 cc. capacity. This bomb could then be disconnected and cooled before releasing the pressure.

Gas was used as a fuel, air being supplied by a fan. Separate valves for gas and air made possible considerable adjustment of gas–

air ratios. The furnace was baffled so as to obtain a fairly long gas travel, the boiler being heated on all sides.

Feedwater was supplied by means of a displacement pump having an adjustable stroke, and driven by means of an induction motor through belt and speed-reducing gears. The source of water for building up the synthetic feeds used was condensed steam collected from radiators used to heat the building, and was stored in a steel barrel. This condensed steam averaged about 170 deg. F. and was practically free from dissolved carbon dioxide. The feed line was projected to the bottom of the barrel and kept it full and at a maximum temperature at all times.

Synthetic feedwater was made up by weight in 100-lb. and 40-lb. lots, the required salts being weighed accurately on an analytical balance.

14. *Procedure in Operating Laboratory Boiler.*—In most tests the boiler was filled about half full with the solution to be used as feed, and was then fired. When the pressure had risen to the correct value, the steam take-off was begun and a sample of boiler water was drawn. The time taken to build up pressure varied for the various tests from ½ hr. to 1½ hr., the latter for the higher pressures. The feed pump was then started and the steam valve manipulated so as to maintain a constant predetermined water level. It generally required an hour to secure the intended steaming rate. The pump was then allowed to run continuously, and being induction-motor driven, ran at approximately constant speed. Steam pressure was maintained by gas-burner adjustment. In general, the water level did not vary more than ¼ in. from normal when samples were drawn, nor the pressure more than 5 per cent. This condition was attained through constant attention of the operator in the early stages of a test.

A careful check was made on the total water fed to the boiler. All tests, unless otherwise specified, were run at the same setting of the pump stroke, but, due to the variation in the volumetric efficiency of the pump and the regulation of the motor, the actual rates varied from about 95 lb. per hour at 150 lb. gage pressure to about 82 lb. per hour at a steam pressure of 1500 lb.

15. *Method of Analysis.*—The amount of boiler water drawn off for each sample varied from 0.4 to 0.6 lb., depending on how well the boiler pressure would fill the bomb. No difference in results was obtained by evacuating the bomb other than obtaining a full bomb each time, so that this procedure was given up. The sampling opera-

tion generally took several minutes, and no noticeable disturbance took place in the boiler. It is felt that a representative sample was obtained, as blowdown samples were identical with those taken from the bomb at the same time. The samples obtained were generally quite clear, although at times an iron-oxide suspension was noticeable. This settled within several hours and did not interfere with analysis. Samples were kept stoppered in flasks awaiting analysis.

Approximately 0.02 *N* hydrochloric acid was used in the ordinary double titration with phenolphthalein and methyl orange as indicators. The modified Winkler barium-chloride method was used as a check. Equal amounts were measured out in a pipette and transferred to separate flasks. The amounts used were such that at least 20 cc. of acid was used to obtain an end-point. For strongly concentrated waters a stronger standardized acid was used, as extreme dilution by the acid makes the methyl-orange end-point difficult to check. To the second sample was added from 5 to 10 cc. of 10–per–cent barium chloride solution. This solution previously had been made alkaline with sodium hydroxide, to set any dissolved carbon dioxide, and then neutralized to the end point of phenolphthalein. The sample was then well shaken and allowed to stand about 5 minutes. It was then titrated with acid, being continuously agitated to avoid acid concentration, to the phenolphthalein end-point. The number of cubic centimeters used gave a measure of the hydroxide content. The results obtained by the two methods checked very closely when only carbonate and hydroxide were present in the boiler water.

With the double-titration method there is a slight tendency to stop short of the true phenolphthalein end-point, giving a slightly higher carbonate content. Where only hydroxide is present, as in the case of the second titration, the end-point is sharply defined. In all of the foregoing titrations care was taken to keep all flasks stoppered and titrations were made as rapidly as possible in order to avoid contamination with carbon dioxide from air and breath. Such contamination increases the carbonate and decreases the hydroxide.

16. *Test Data and Discussion of Results.*—The amounts of sodium hydroxide and sodium carbonate in a boiler water, if expressed as sodium carbonate and arranged in the ratio

$$\frac{\text{NaOH as } Na_2CO_3}{(\text{NaOH plus } Na_2CO_3) \text{ as } Na_2CO_3}$$

express the degree to which decomposition has proceeded, if all of the sodium hydroxide may be assumed to have originated from the carbon-

ate. This ratio may be expressed as per cent decomposition plotted against time and against total boiler water alkalinity. Well-defined smooth curves were obtained. Figure 8a shows the series obtained from the tests using 400 parts per million sodium carbonate in the feedwater. It is apparent that a balance or equilibrium is soon established between the decomposition rate and the incoming sodium carbonate. The maximum per cent decomposition was obtained about two hours after steaming was started, decomposition thereafter decreasing steadily with increase in boiler-water concentration. It is noticeable that the higher pressures have proportionately less effect than the lower pressures. In all of these tests slightly over two concentrations occurred per hour.

Figure 8b was obtained from tests using 150 parts per million sodium carbonate, and shows a similar balance after a somewhat longer time. Figure 8c was obtained from a 50 parts per million feed. The extremely slow approach to equilibrium is noticeable, especially so at the higher pressures. The irregular building up is probably due to failure to exactly duplicate the steaming rates during the first hour or so. Had these tests been run for a longer time, the maximums would undoubtedly have been more clearly defined. As might be expected, the decomposition is higher for this purer feedwater, and operating pressure becomes less a factor.

It was not advisable to run a similar test with a still purer water because of the time required to build up an appreciable concentration. Therefore the boiler was charged with a more concentrated solution at the start, and a 10-parts-per-million feed of sodium carbonate begun. Two such tests were run, the initial charges being 500 parts per million and 4000 parts per million sodium carbonate. The maximum percentages of decomposition obtained were 91.5 and 90.4, respectively, with an operating pressure of 250 lb. A change in pressure to 500 lb. caused an increase of 1.2 per cent in the first test. Untreated water was then fed for five hours in the latter test, the decomposition rising to 94.2 per cent as an average for the last three hours.

In most tests a slight loss in boiler-water alkalinity was noticeable. Condensed steam from the boiler showed from 10 to 20 parts per million methyl-orange alkalinity expressed as sodium bicarbonate, indicating some carry-over. This did not change appreciably with boiler-water concentration. The presence of a few small leaks in connections below the water level at high pressures, and the possibility of the baking of the salt on the surface above the water level may

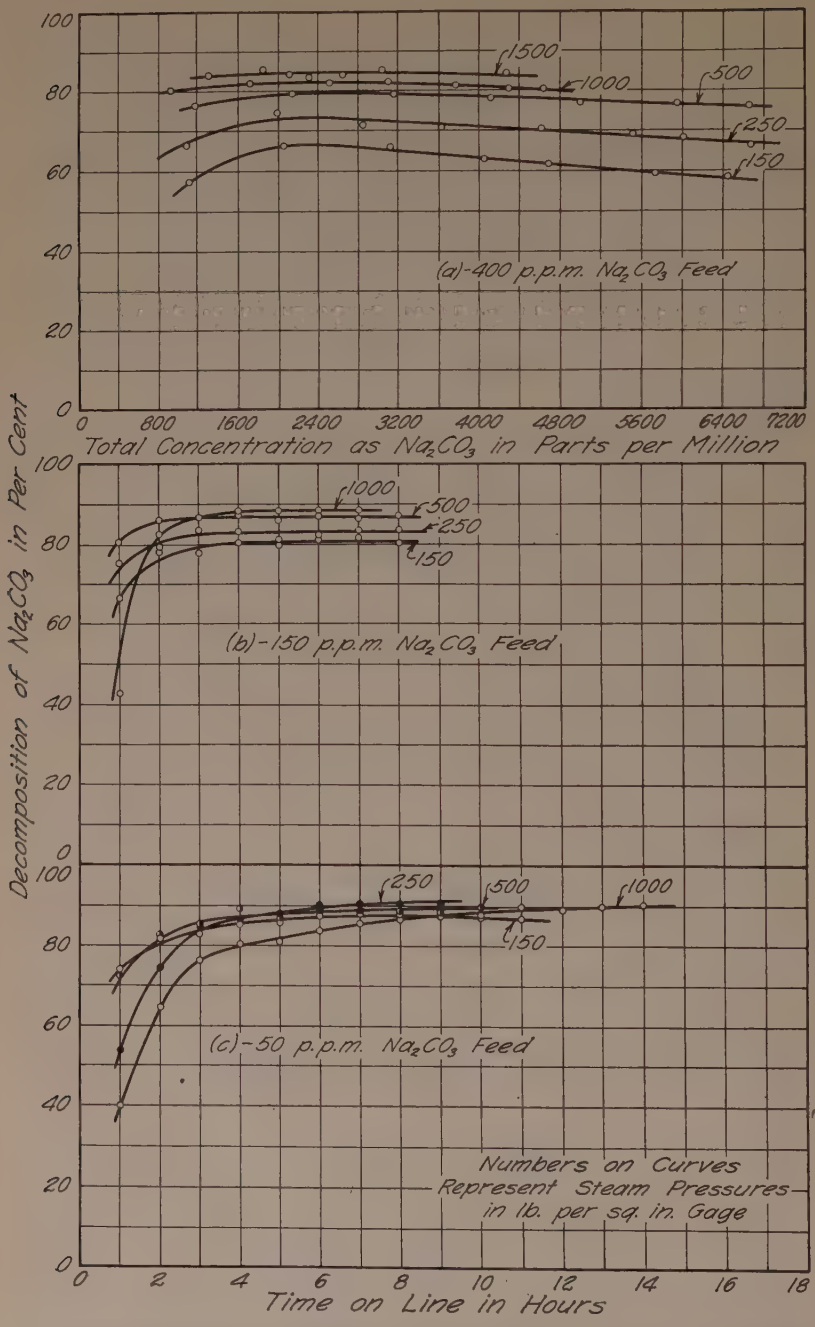
Decomposition of Na_2CO_3 in Per Cent
Total Concentration as Na_2CO_3 in Parts per Million
Time on Line in Hours
(a)-400 p.p.m. Na_2CO_3 Feed
(b)-150 p.p.m. Na_2CO_3 Feed
(c)-50 p.p.m. Na_2CO_3 Feed
1500
1000
500
250
150
Numbers on Curves Represent Steam Pressures in lb. per sq. in. Gage

FIG. 8. DECOMPOSITION OF Na_2CO_3 FOR 400, 150, AND 50 P.P.M. Na_2CO_3 FEED

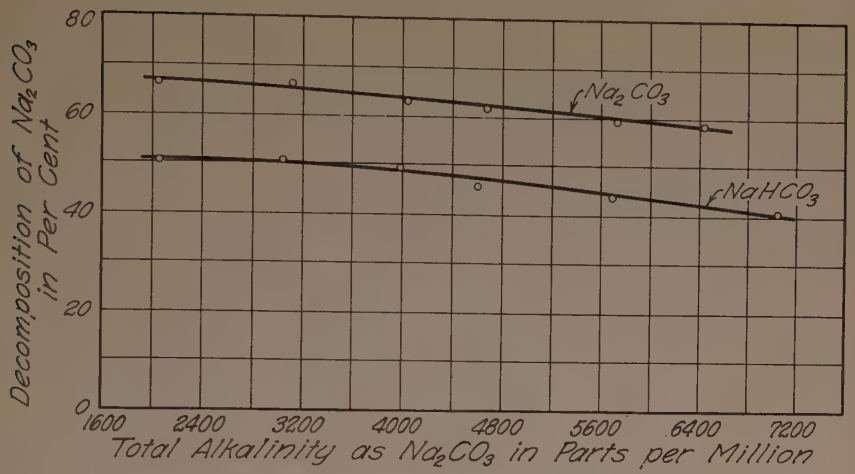

FIG. 9. EFFECT OF PARTIAL PRESSURE OF CO_2 ON DECOMPOSITION OF Na_2CO_3, AT 150-LB. STEAM PRESSURE, WITH 400 P.P.M. FEED

account for the fact that total alkalinity actually decreased when 10 parts per million sodium carbonate was fed.

It was noticed in several tests that a sample drawn while the water level was falling would show a higher decomposition, and one drawn with a rising water level the opposite, the rate coming back to normal when the water level was kept constant. This would indicate an equilibrium controlled by the partial pressure of the carbon dioxide in the steam space. A test was therefore run with sodium bicarbonate only in the feed, and in quantity sufficient to give the same sodium concentration, but twice the amount of available carbon dioxide. Figure 9 gives the results obtained and indicates that the amount of available carbon dioxide in the feedwater, and consequently the partial pressure of carbon dioxide in the steam space, is a controlling factor.

A steady decrease in decomposition with increase in total alkalinity of the boiler water is especially noticeable in the case of 400-parts-per-million feedwater. Later tests revealed the same dropping-off tendency in the case of 150-parts-per-million sodium carbonate in the feedwater, but to lesser extent. This would indicate that total alkalinity or possibly sodium-hydroxide alkalinity alone was a factor. Several tests were run at various concentrations, keeping the total alkalinity constant with various amounts of blowdown ranging from 4 to 30 per cent. It was noticed that while the total alkalinity was kept constant, the decomposition also became constant, and conse-

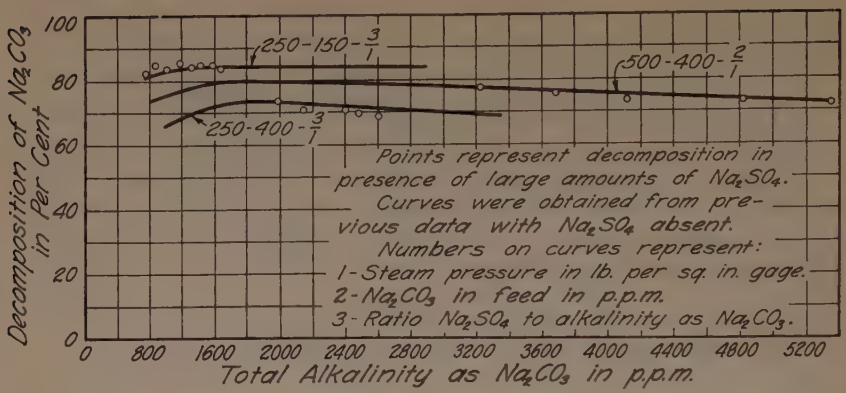
Decomposition of Na_2CO_3 in Per Cent
100
80
60
40
20
0
250-150-3/1
500-400-2/1
250-400-3/1
Points represent decomposition in presence of large amounts of Na_2SO_4.
Curves were obtained from previous data with Na_2SO_4 absent.
Numbers on curves represent:
1-Steam pressure in lb. per sq. in. gage.
2-Na_2CO_3 in feed in p.p.m.
3-Ratio Na_2SO_4 to alkalinity as Na_2CO_3.
0 800 1600 2000 2400 2800 3200 3600 4000 4400 4800 5200
Total Alkalinity as Na_2CO_3 in p.p.m.

FIG. 10. DECOMPOSITION OF Na_2CO_3 IN PRESENCE OF LARGE AMOUNTS OF Na_2SO_4

quently the sodium-hydroxide concentration was kept constant. A heavy blow-down, such as was necessary at a low boiler-water concentration, was accompanied by a decrease in decomposition. This was to be expected, as the blowdown also carries out carbonate undecomposed, and if increased to the limiting case, or 100 per cent, would result in a decomposition approaching zero. A 30-percent blowdown with a 150-parts-per-million feed reduced the decomposition about 6 per cent, and a 7½-per-cent blowdown reduced the decomposition about 1.2 per cent, both at 250 lb. operating pressure.

To determine whether the addition of large amounts of inert soluble salts (increase in ionic strength*) such as sodium sulphate or chloride might be a controlling factor, several tests were run with large quantities of sodium sulphate added to the feedwater. Figure 10 shows the plotted results of such tests. The curves were drawn from previous data obtained using sodium carbonate alone. The fair agreement indicates that total ionic strength has but slight effect over the ranges run in these tests. The maintenance of the A.S.M.E. ratios of sulphate to alkalinity should not appreciably affect the decomposition that can be expected.

Early in the schedule of testing several runs were made with different rates of steaming. Figure 11 gives the results obtained, and indicates that boiler rating alone has little effect on decomposition, and is not a factor in these accelerated tests. An additional high-steaming-rate test was run with 400-parts-per-million feed, and showed fair agreement with a previous low-rate test.

*Lewis and Randall, "Thermodynamics." McGraw-Hill Book Co. 1931.

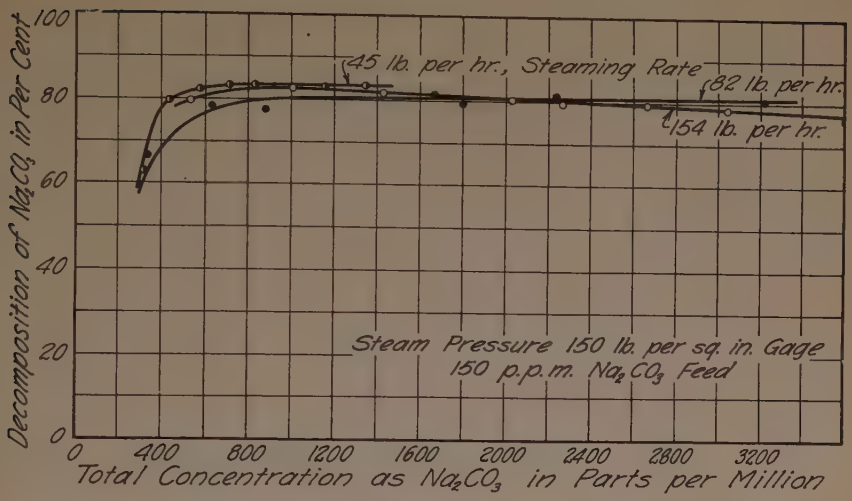

FIG. 11. DECOMPOSITION OF Na_2CO_3 AT VARIOUS STEAMING RATES

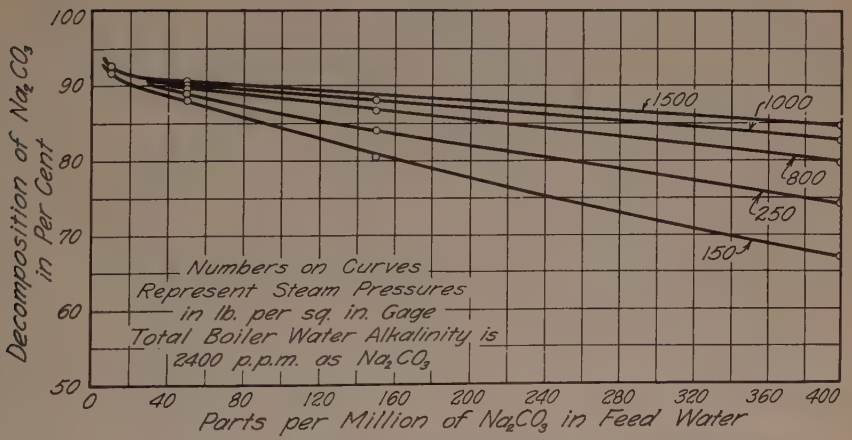

FIG. 12. MAXIMUM DECOMPOSITION OF Na_2CO_3 FOR VARIOUS PRESSURES AND COMPOSITIONS OF FEEDWATER
Total boiler water alkalinity, 2400 p.p.m. as Na_2CO_3

An attempt was made to correlate decomposition data for various pressures and compositions of feedwater, for some particular boiler-water concentration that might be maintained by means of blowdown. The curves in Fig. 12 were drawn from selected data on decomposition at about 2400 parts per million total boiler-water alkalinity ex-

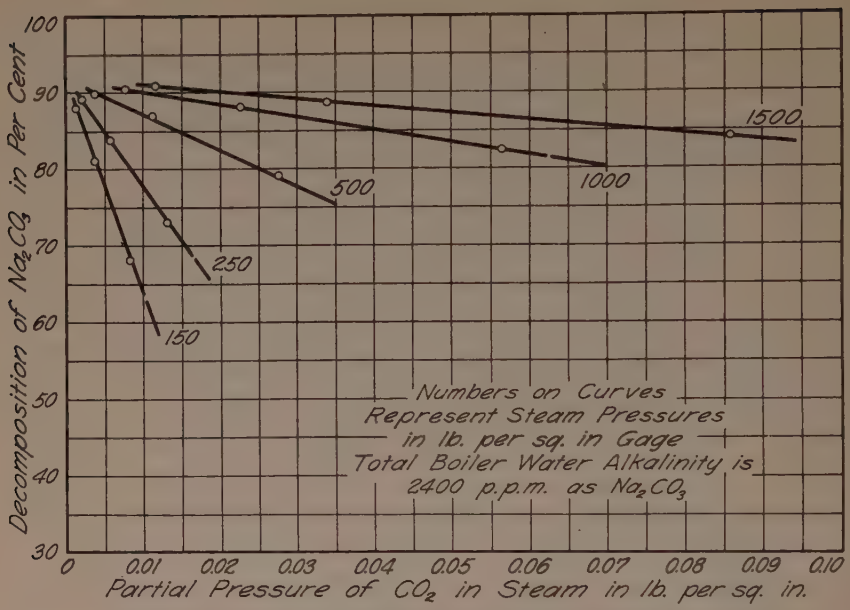

FIG. 13. EFFECT OF PARTIAL PRESSURE OF CO_2 ON DECOMPOSITION OF Na_2CO_3, AT VARIOUS STEAM PRESSURES

Total boiler water alkalinity, 2400 p.p.m. as Na_2CO_3

pressed as sodium carbonate. The curves are extrapolated somewhat on the assumption that decomposition would approach 100 per cent for a very pure feedwater. A similar family of curves might be drawn for a higher boiler-water concentration or alkalinity, and also for a lower total alkalinity, differing somewhat at higher feedwater concentrations of carbonate, but very little for feedwaters containing very little sodium carbonate.

Such a chart as Fig. 12 might be useful in estimating decomposition and in checking boiler-water analyses, unless there exist other factors of equal importance that have not been investigated. The curves are based on the attainment of equilibrium previously referred to, a condition which may not always occur in the operating boiler at all times. Quick or sudden changes in steaming rate of great magnitude and intermittent blowdown are probably factors.

Figure 13 was obtained from a calculation of the partial pressure of carbon dioxide in the steam based on decomposition data at a total alkalinity of 2400 parts per million. The curves are drawn as straight lines that converge at a point, indicating about 92 per cent decomposition at zero partial pressure. Theoretically, the decomposition should proceed to 100 per cent completion on the reduction of

the partial pressure of the carbon dioxide to zero, and with sufficient time. However, removing the carbon dioxide is a dilution process and very slow in the last stages. It appears that a small amount of carbon dioxide has at this point tremendous effect on the completion of this reaction, and the practical limit of decomposition from a feedwater containing but very little potential carbon dioxide seems to be from 92 to 94 per cent.

To check this, two tests were run, using for a feedwater the purest water available—namely, that used in making up these various synthetic solutions. This water showed a methyl-orange alkalinity equivalent to 10 parts per million sodium carbonate, but an accurate carbon-dioxide evolution test accounted for only 5 parts per million expressed as sodium carbonate. Starting with a maximum decomposition of 91.5 per cent obtained with a 10-parts-per-million feed at 250 lb. pressure, the pure water was fed to the boiler for two hours. The final sample drawn showed a decomposition of 93.7 per cent at a total boiler-water alkalinity of 321 parts per million. A second similar test was started with a decomposition of 90.4 per cent similarly obtained, and regular steaming was continued for five hours. The last three samples were almost the same and averaged 94.2 per cent decomposition at a boiler-water alkalinity of 3500 parts per million.

No chemical reaction is absolutely instantaneous, but requires some time. Under some conditions the time required may approach zero. Usually in the early stages the speed is very high, but as completion is approached and the amount of reacting substance becomes small, the speed decreases considerably. Even under favorable conditions the reaction may require considerable time for completion. Judging from this line of reasoning, it may be possible in the rapidly-steaming modern high-pressure boiler, where as many as fifteen concentrations may occur in an hour, that the decomposition rate for a very pure water may be exceeded, and sodium carbonate accumulate in the boiler faster than it can decompose to maintain an equilibrium dependent upon the partial pressure of the carbon dioxide. Such a boiler would show a lower decomposition, and this may be the reason for the low decomposition occurring in some boilers. In the test boiler a change of from one concentration per hour to almost four per hour did not produce any appreciable drop in decomposition.

Most of the boiler-water data that the author has examined show percentages of decomposition lower than that predicted by the curves on Fig. 12, or that might be predicted at some other boiler-water

alkalinity corresponding to the case at hand. There are various ways that this may occur. The use of insufficient lime in a lime-soda plant may leave bicarbonates in the water, which might be interpreted as carbonate. Some plants treat the water with carbon dioxide after passing the softening plant to prevent precipitation of the normal carbonate in the feed lines and heater.

The methods used for determination of carbonate and hydroxide in the average boiler plant are open to error. The presence of certain organic matter in a boiler water is known to displace the methyl-orange end-point and to cause too high carbonate to be indicated. In the presence of sodium sulphate the methyl-orange end-point is not so easily defined, is likely to be exceeded, and to give too high an indication of carbonate. The Winkler barium-chloride method in the presence of sodium sulphate gives too low an indication of hydroxide. In all, the ordinary methods are likely to give too low an indication of decomposition. The direct method of breaking down the carbonates and absorbing the carbon dioxide evolved is tedious and hardly adapted to boiler-plant routine.

Some plants have reported decomposition higher than 95 per cent. Such a case might occur in a central station using a small evaporated make-up. However, overtreatment with lime in a lime-soda softening plant would result in such a boiler water, high in hydroxyl ion and giving an indication of a higher decomposition than actually exists. A recent test with sodium hydroxide also in the water gave a decomposition several per cent higher than that which could be predicted from the sodium carbonate alone.

The foregoing tests were performed primarily to obtain data comparable with such as might be expected from an operating industrial boiler, and to gain a knowledge of the factors affecting this decomposition phenomenon. The equilibrium or balance referred to is not the usual equilibrium of the reaction, but represents a balance of the effects of the carbonate coming in with the feedwater, the carbon dioxide leaving with the outgoing steam, and the sodium hydroxide accumulating in the boiler water. The usual chemical equilibrium, while dynamic in theory, is static in regard to the total amount of reacting substances.

A comparison of data obtained under these two states seemed desirable in the hope that equilibrium constants and activity coefficients* might be helpful in explaining and predicting decomposition in the average boiler. No applicable quantitative data on this reaction were

*Lewis and Randall, "Thermodynamics." McGraw-Hill Book Co. 1931.

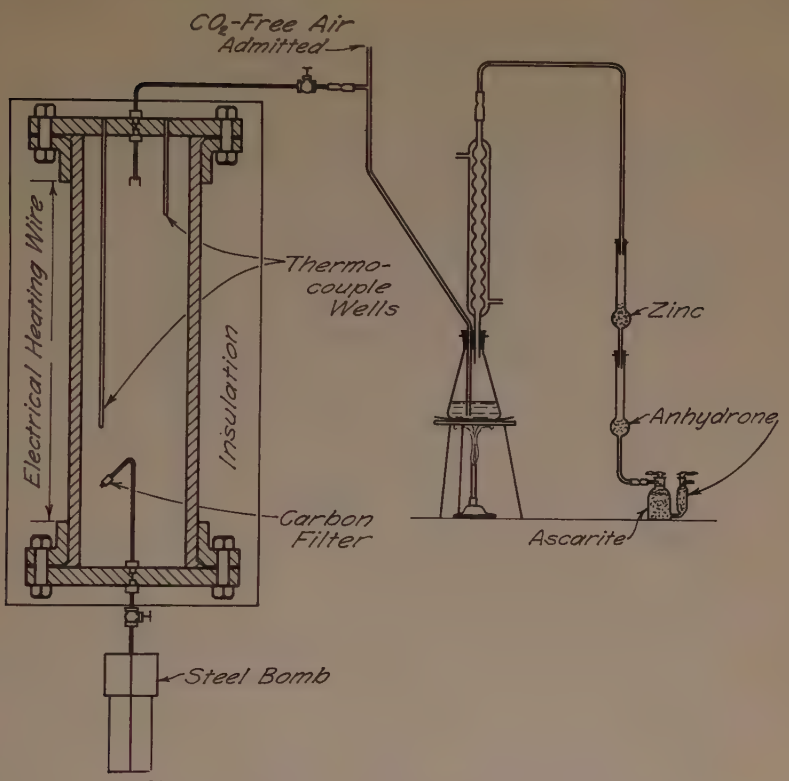

FIG. 14. ESSENTIALS OF EQUILIBRIUM APPARATUS

available. A second series of tests was therefore performed to obtain true equilibrium data for this reaction. In these tests equilibrium conditions were established, small samples of steam and water were slowly withdrawn for analysis, and the whole procedure conducted so as to create the least disturbance within the boiler.

17. *Apparatus Used for Equilibrium Tests.*—An electrically-heated vessel of approximately 42 000 cc. was charged with solutions of various proportions of sodium hydroxide and sodium carbonate and heated to various temperatures. The amounts of solution charged varied from 22 to 38 kg., leaving a space above the solution for steam formation and the accompanying carbon dioxide. The boiler thus formed was so arranged that steam could be slowly withdrawn, and a sample of water run off through a filter at the bottom into a steel bomb, cooled, and analyzed at room temperature. The essential apparatus is shown in Fig. 14. The amounts of steam withdrawn varied from 300 to 900 grams, and the rate of withdrawal was varied from 3 to 10 grams per minute.

18. *Methods of Analysis.*—

(a) CO_2 Determination

The steam withdrawn was passed directly into an Erlenmeyer flask and kept boiling by a gas burner. A refluxing condenser was used to retain the condensed steam and pass on the noncondensable gases. These were passed through granulated zinc to take out any hydrogen sulphide originating in the rubber connections, dried by passing through anhydrone, and finally passed through a Wesson bulb containing ascarite and anhydrone to absorb the carbon dioxide. Carbon dioxide-free air was bubbled into the Erlenmeyer flask beneath the water level, and a few drops of strong acid were added to aid in the complete evolution of any carbon dioxide. For very small quantities of carbon dioxide—that is, less than 20 mg.—the gases were bubbled through a Meyer's sulphur bulb containing 0.02 *N* barium hydroxide, and the carbon dioxide determined by titration with 0.02 *N* hydrochloric acid to the phenolphthalein end point.

(b) Determination of Hydrate and Carbonate Content of Boiler Water

The water analyses were made using three methods: the A.P.H.A. method, using phenolphthalein and methyl-orange indicators; the Winkler method, using barium chloride to precipitate out the carbonates; and the carbon dioxide-evolution method by acidification to determine carbonates. These methods for the most part checked very well within the experimental error involved. The evolution method was found most reliable.

19. *Test Data and Discussion of Results.*—The data obtained are given in Table 12. The constants *K*, *K'*, and *K''* were calculated as

TABLE 12
RESULTS OF TESTS IN EQUILIBRIUM BOILER

Test	Temperature deg. F.	NaOH mm. per liter	Na_2CO_3 mm. per liter	Ionic Strength mm. per liter	Decomposition per cent	CO_2 p.p.m.	Partial Pressure CO_2 Atmos. $\times 10^{-4}$	K $\times 10^{-4}$	K' $\times 10^{-4}$	K'' $\times 10^{-4}$
30	296	40.3	2.99	49.27	87	18.2	0.329	179.0	4.44	1.01
39	296	29.0	9.25	56.75	61	65.5	1.19	108.2	3.72	0.84
50	365	6.19	1.735	11.4	63.6	230.0	10.54	232.0	37.6	3.37
50	365	5.86	1.9	11.56	60.7	230.0	10.54	190.4	32.5	2.90
35	365	43.5	2.05	49.7	91.4	21.5	0.987	91.0	21.0	1.87
35	365	44.0	1.91	49.8	92.3	21.5	0.987	100.0	22.7	2.02
29	365	41.0	2.945	49.84	87.5	46.2	2.12	121.0	29.5	2.63
23	365	26.8	7.55	49.45	61.1	194.2	8.81	83.9	31.3	2.79
22	365	26.15	7.8	49.6	59.9	204.0	9.40	82.4	31.5	2.81
42	365	17.45	14.51	60.98	37.6	360.0	16.52	34.7	19.9	2.24
42	365	20.5	14.0	62.5	40.0	360.0	16.52	49.6	24.2	2.16
66	365	51.9	17.45	104.25	59.8	146.0	6.7	.....	20.2	1.80

TABLE 12
RESULTS OF TESTS IN EQUILIBRIUM BOILER (Concluded)

Test	Temperature deg. F.	NaOH mm. per liter	Na_2CO_3 mm. per liter	Ionic Strength mm. per liter	Decomposition per cent	CO_2 p.p.m.	Partial Pressure CO_2 Atmos. $\times 10^{-4}$	K $\times 10^{-4}$	K' $\times 10^{-4}$	K'' $\times 10^{-4}$
4–28	406	5.9	1.98	11.84	59.4	298.0	20.2	357.0	60.2	3.34
4–30	406	7.6	1.47	12.01	72.5	185.0	13.6	534.0	70.5	3.90
C	406	19.8	3.3	29.7	75	171.0	12.6	1500.0	75.5	4.19
A	406	24.15	3.02	33.21	80	129.0	9.53	1840.0	76.1	4.22
B	406	28.8	2.75	37.05	84	80.0	5.91	1785.0	62.0	3.44
6–25	406	33.6	2.17	40.11	88.6	28.2	3.04	1580.0	47.1	2.61
33	406	42.2	1.56	46.88	92.4	33.0	2.44	2780.0	66.0	3.66
4–13–J	406	22.01	9.0	49.0	55.0	365.0	27.0	1450.0	66.0	3.66
28	406	41.0	2.83	49.49	88.1	70.0	5.18	3080.0	75.0	4.16
4–14–I	406	23.0	9.1	50.3	56.0	348.0	25.7	1490.0	59.0	3.27
37	406	25.6	9.54	54.22	57.5	280.0	20.65	1420.0	55.6	3.14
4–7–K	406	28.6	8.91	55.33	61.7	232.0	17.2	1580.0	55.2	3.06
E	406	32.6	8.4	57.8	66	203.0	14.96	1890.0	58.0	3.22
54	406	18.25	13.41	58.48	40.5	516.0	38.1	947.0	51.9	2.88
41	406	16.96	13.97	58.87	37.8	543.0	40.1	825.0	48.7	2.70
25	406	46.7	5.94	64.52	79.4	116.0	8.55	3140.0	67.2	3.73
D	406	44.7	7.83	68.19	74	120.0	8.85	2260.0	50.5	2.80
F	406	61.6	8.3	86.5	79	80.3	5.91	2710.0	43.9	2.44
65	406	49.1	18.5	104.6	57.0	209.0	15.4	.....	40.9	....
G	406	80.0	9.06	107.2	81.6	42.7	4.5	3180.0	39.8	2.21
57	469	4.45	1.54	9.1	59.0	375.0	53.7	690.0	155.0	4.42
18	469	8.5	0.283	9.35	93.3	44.5	6.4	1630.0	192.0	5.48
17	469	7.93	0.49	9.4	89.0	61.7	8.85	1136.0	143.0	4.08
16	469	7.65	0.623	9.52	85.0	88.4	12.86	1210.0	158.0	4.50
15	469	6.05	1.237	9.76	71.2	149.0	20.6	610.0	101.0	2.88
13	469	2.73	2.357	9.8	36.6	616.0	88.0	278.0	102.0	2.88
14	469	4.51	1.82	9.97	55.4	358.0	42.4	475.0	128.0	3.65
3	469	18.7	0.834	20.7	91.7	83.6	12.0	5040.0	269.0	7.65
9	469	14.0	2.22	20.66	76.0	271.0	39.0	3440.0	246.0	7.02
11	469	15.45	1.932	21.25	80.0	191.6	27.5	3380.0	220.0	6.28
12	469	16.0	1.791	21.37	81.6	170.0	24.4	3490.0	218.0	6.22
7–8	469	23.1	0.32	24.1	97.0	14.3	2.04	3400.0	147.0	4.20
6	469	23.05	0.557	24.72	95.2	20.6	2.95	2820.0	122.0	3.48
32	469	41.0	1.49	45.47	93.2	58.0	8.24	9300.0	226.0	6.45
27	469	41.4	2.76	49.68	88.2	117.0	16.7	10370.0	250.0	7.14
19	469	22.9	9.72	52.06	53.5	543.0	77.8	4400.0	183.0	5.22
20	469	26.2	9.08	53.44	59.0	505.0	72.5	5490.0	209.0	5.96
36	469	26.1	9.21	53.73	58.6	451.0	64.6	4920.0	183.0	5.22
36	469	25.8	9.35	53.85	56.8	451.0	64.6	4600.0	178.0	5.08
53	469	17.45	13.3	57.35	39.7	762.0	109.8	2520.0	144.0	4.11
21	469	31.75	8.94	58.57	64.0	429.0	61.5	6930.0	218.0	6.22
40	469	17.1	13.85	56.65	38.1	816.0	116.9	2470.0	144.0	4.11
40	469	15.7	14.55	59.35	35.0	816.0	116.9	1980.0	126.0	3.59
26	469	51.1	6.09	69.37	80.6	172.0	24.7	10600.0	207.0	5.9
63	469	46.6	17.1	97.84	58.0	334.0	47.6	6050.0	130.0	3.71

Test	Temperature deg. F.	NaOH mm. per liter	Na_2CO_3 mm. per liter	Na_2SO_4 mm. per liter	Ionic Strength mm. per liter	Decomposition per cent	CO_2 p.p.m.	Partial Pressure CO_2 Atmos. $\times 10^{-4}$	K $\times 10^{-4}$	K' $\times 10^{-4}$	K'' $\times 10^{-4}$
50	365	6.2	1.735	10.5	42.7	63.6	230.0	10.53	234.0	37.6	3.37
46	365	35.6	5.56	63.6	243.1	76.2	62.0	2.84	647.0	18.4	1.64
48	406	4.66	2.36	10.11	41.07	49.8	424.0	31.5	290.0	62.2	2.43
51	406	6.05	1.8	10.5	42.7	62.7	306.0	22.6	460.0	76.0	2.96
45	406	36.1	5.14	63.1	240.8	77.9	132.0	9.74	2470.0	68.5	2.67
49	469	5.5	1.91	10.11	41.56	59.0	460.0	66.0	1045.0	190.0	5.42
52	469	7.14	1.31	10.6	43.0	73.0	289.0	41.5	1610.0	226.0	6.45
43	469	34.1	5.21	60.5	231.2	76.6	217.0	31.0	6920.0	203.0	5.80
44	469	34.5	5.2	61.0	233.1	77.0	194.0	27.9	6400.0	185.0	5.29
47	469	37.3	5.1	64.5	244.6	78.5	188.0	26.9	7350.0	197.0	6.52

follows, using mole fractions and partial pressure of carbon dioxide in atmospheres (P_{CO_2}):

$$\frac{(NaOH)^2 \times P_{CO_2}}{Na_2CO_3} = K \qquad \frac{NaOH \times P_{CO_2}}{Na_2CO_3} = K' \qquad \frac{NaOH \times CO_2}{Na_2CO_3} = K''$$

In order to compare these data with data on the previous boiler tests, the corresponding percentage decomposition was also calculated. In the latter portion of the table are given data obtained on experiments in which large amounts of sodium sulphate were added to increase the ionic strength. In this range ionic strength, as in the operating boiler test, seems to have little influence.

There appears to be considerable inconsistency in the constants calculated. On the basis of reaction (2), (see p. 32) K should be the equilibrium constant if activities could be disregarded. This constant would include the ratio of activities. The inconsistencies do not appear to be influenced by ionic strength; consequently, activities are probably not an important factor. It appears that reaction (2) is not adequate.

An investigation was made of the possibility of the existence of appreciable amounts of bicarbonate ion in the boiler water. At room temperature the reaction represented by

$$Na_2CO_3 + H_2O \rightleftarrows NaOH + NaHCO_3 \qquad (3)$$

is known to be displaced far to the left, and the amounts of bicarbonate existing are very low. A calculation of free energy* indicates this to be true, and also indicates that the reaction may be reversed and displaced to the right with increase in temperature. This points to the probable existence of considerable amounts of bicarbonate in a boiler water, and this probably is an important factor. The carbonate and hydroxide, as determined in these tests and in all other boiler water analyses, are the quantities after the equilibrium of reaction (3) has been disturbed by cooling and releasing the pressure. The bicarbonate has thereby been reduced, with a resultant increase in normal carbonate at the expense of the hydroxide. They are the factors of equilibrium at room temperature and may differ considerably from those at boiler temperatures. This may account for some of the inconsistency in the data and results.

It was noticeable that in the steaming boiler the percentage decomposition apparently reached a maximum value of about 95 per

*Lewis and Randall, "Thermodynamics." McGraw-Hill Book Co., 1931.

TABLE 13

MAXIMUM DECOMPOSITION OF SODIUM CARBONATE OBTAINABLE WITH VARYING COMPOSITION OF FEEDWATER

Temperature, 406 deg. F.

No.	Elapsed Time, hr.	NaOH	Na_2CO_3	Alkalinity	Decomposition per cent
			Feed 150 p.p.m.		
1	0.75	2415	660	3860	82.9
2	1.25	2450	710	3930	82.0
3	1.75	2610	750	4210	82.1
4	2.25	2680	750	4300	82.6
			Feed 50 p.p.m.		
5	2.75	2563	680	4080	83.4
6	3.25	2620	660	4130	84.0
7	3.75	2830	560	4300	87.0
8	4.25	2650	510	4020	87.2
9	4.75	2790	550	4240	87.2
			Feed 10 p.p.m.		
10	5.25	2640	400	3900	89.6
11	5.75	2720	390	3990	90.4
			Feed Distilled Water About 5 p.p.m. CO_2		
12	6.25	2570	280	3680	92.5
13	6.75	2640	245	3745	93.5
14	7.75	2515	220	3550	93.8
15	8.75	2565	180	3580	95.0
16	9.75	2460	190	3450	94.5
17	10.50	2200	210	3120	93.5

cent, beyond which it was very difficult to go. In Table 13 are given data indicating the maximum decomposition attainable for various feed water concentrations. The distilled water fed during the last five hours was the purest water available in large quantities—namely, condensate from the radiators in the building. It had a very slight methyl orange alkalinity, and a carbon dioxide-evolution test disclosed a maximum of about 5 parts per million of carbon dioxide. It is probable that the maximum decomposition attainable would be slightly higher if an absolutely carbon dioxide-free water were used. Since determination of carbonate by titration methods is in this range difficult and open to error, another test was run to check the titrations with the evolution method for carbonates, the hydroxide being determined by difference. Table 14 gives the data obtained, which substantially checks the data in Table 13. These tests tend to affirm the existence of a bicarbonate content difficult to break down or dissipate.

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TABLE 14

MAXIMUM DECOMPOSITION OF SODIUM CARBONATE OBTAINED USING DISTILLED WATER AS FEED

(Solution added to boiler at start contained 120 p.p.m. Na_2CO_3 and 1720 p.p.m. NaOH Temperature, 406 deg. F.)

No.	Elapsed Time, hr.	NaOH	Na_2CO_3	Alkalinity	Decomposition per cent
1	0.5	1760	120	2450	95.1
2	1.5	1562	71	2140	96.7
3	3.5	1420	83	1960	95.8
4	4.25	1700	88	2345	96.2
5	5.25	1263	91	1776	94.9

The author knows of no simple and sure way to detect bicarbonate in the presence of hydroxide at boiler temperatures, although with sufficient data it may be possible to calculate the amount. On the assumption that the bicarbonate is proportional to the partial pressure of the carbon dioxide in the vapor phase, the constants K' have been calculated from reaction (3) thus:

$$\frac{\text{NaOH} \times P_{CO_2}}{Na_2CO_3} = K'$$

using mole fractions of carbonate and hydroxide as analyzed. Considerable grouping of the constants occurs, thereby indicating that reaction (3) is probably the controlling reaction. Using mole fractions of carbon dioxide instead of partial pressures gives the constants K'' in which the pressure variation in the constant K' is eliminated. The variation of constants K'' should be that due to temperature only, provided correct data could be used in their calculation.

Using data obtained from the laboratory operating boiler, constants K' and K'' were calculated and the results obtained are shown in Table 15. The partial pressure of carbon dioxide was calculated from the decomposition data and not from direct quantitative measurements of carbon dioxide. It is interesting to note that these constants fall within the ranges covered by the equilibrium constants, although their numerical values are in general slightly lower. This would suggest that the decomposition rate is so rapid that an equilibrium condition is approached even in an operating and steaming boiler.

20. *Conclusions.*—Based on this investigation, the following conclusions may be drawn:

(1) The principal controlling factor in establishment of the extent of decomposition of sodium carbonate in a boiler water is the partial pressure of the carbon dioxide in the vapor phase. This in

TABLE 15

RESULTS OF TESTS IN LABORATORY OPERATING BOILER

Feed Na_2CO_3 p.p.m.	Temperature deg. F.	Decomposition per cent	Ionic Strength	NaOH	Na_2CO_3	Partial Pressure CO_2, atmos. $\times 10^{-4}$	$K' \times 10^{-4}$	$K'' \times 10^{-4}$
			millimoles per liter					
400	372	67.5	52.68	30.6	7.36	5.66	23.5	1.92
400	406	73.0	52.1	33.1	6.34	8.92	46.6	2.58
400	469	79.0	50.1	35.8	4.75	18.8	142.0	4.05
400	372	65.0	71.0	39.3	10.58	5.41	20.1	1.645
400	406	72.5	68.7	43.8	8.30	8.89	46.5	2.60
400	469	79.0	66.8	47.7	6.35	18.8	141.0	4.03
400	372	63.5	89.4	48.0	13.8	5.28	18.4	1.50
400	406	71.0	86.3	53.6	10.9	8.7	42.7	2.37
400	469	78.0	83.8	58.9	8.3	18.6	132.0	3.76
400	372	61.0	108.3	55.2	17.7	5.08	16.5	1.35
400	406	70.0	104.3	63.5	13.6	8.6	40.0	2.22
400	469	77.5	100.8	70.2	10.2	18.4	127.0	3.62
150	372	81.0	49.6	36.7	4.3	2.57	22.0	1.795
150	406	84.0	48.9	38.0	3.62	3.86	40.5	2.25
150	469	87.0	48.2	39.4	2.94	7.77	104.0	2.98
50	372	88.0	48.0	39.8	2.72	0.915	13.4	1.09
50	406	89.0	47.7	40.3	2.49	1.36	22.0	1.22
50	469	89.7	47.6	40.6	2.33	2.68	46.7	1.33

turn depends on the amount and availability of the potential carbon dioxide contained in the feedwater.

(2) The effect of boiler operating pressure decreases with a decrease in carbonate content of the feedwater.

(3) For the range of steaming rates covered in these tests, boiler rating does not appear to be a factor governing the extent of decomposition.

(4) The total alkalinity existing in a boiler water is a factor, the extent of decomposition decreasing with increase in boiler-water alkalinity.

(5) The decomposition phenomenon appears to take place in two steps as expressed by the following:

$$Na_2CO_3 + H_2O \rightleftarrows NaOH + NaHCO_3$$
$$NaHCO_3 \rightleftarrows NaOH + CO_2.$$

(6) Complete or one-hundred-per-cent decomposition cannot be attained even in the steaming boiler.

(7) The usual boiler water analysis indicates less hydroxide than probably exists in the boiler during operation.

IV. SCALE FORMATION IN LABORATORY BOILER

21. *Apparatus for Test of Scale Formation.*—The data reported in Chapter II indicated the solid and liquid phases which would be desir-

able for high-pressure boiler operation. However, they were solubility measurements made under conditions approaching equilibrium in the absence of steam generation. Consequently, the direct application of these data to boiler operation without correlation with data from a steaming boiler might give undesirable results. In order to obtain this correlation, a small one-tube steaming boiler was built. The boiler was built so that a maximum heat transfer of 100 000 B.t.u. per sq. ft. per hr. through the heating tube could be attained. The concentration of the boiler water was made independent of the rate of steam generation, and tests could be run up to the critical temperature. Scale was formed on the heating tube. This scale was analyzed, and the conditions under which the scale could be formed, removed or prevented were studied. Consequently the boiler was called a "scaling boiler."

The "scaling boiler" is shown in Fig. 15. The tube *A* was heated by means of No. 14 Chromel A resistance wire wound around it with a layer of alundum cement about $\frac{1}{16}$ in. thick separating the wire from the tube. Figure 16 shows the heating tube after the resistance wire was wound and before the top layer of cement was applied. The energy input at the tube was measured by means of a kilowatt-hour meter, the rate of energy input being between 2 and 3.5 kilowatts. The drum was insulated with magnesia and heated by means of resistance wire. The amount of heat added at the drum was just enough to compensate for radiation. Thus the heat added at the tube was practically all utilized to generate steam. The steam generated was taken off from the top of the drum by means of a pipe *B*, which connects to the bottom of the water column. A pipe *C* surrounded the steam pipe, and a small amount of water was introduced into this pipe. This acted as a condenser, condensing the steam on the inside and boiling the water on the outside, which was at atmospheric pressure. The steam formed was condensed by means of glass condensers *D* and the condensed steam returned to the jacket surrounding the steam pipe. The amount of steam being condensed in the main steam line was adjusted so that it just balanced the steam being generated in the heating tube. This maintained a constant pressure in the boiler.

By returning the condensed steam to the boiler there was no change in concentration of chemicals in the boiler water and the chemical concentration, in the absence of chemical reaction, remained constant and independent of the rate of steam generation.

The water level was observed by means of a gauge column *E*. The water was introduced into the boiler by means of a plunger-type pump *F*. The pump had two plungers and could be so arranged that

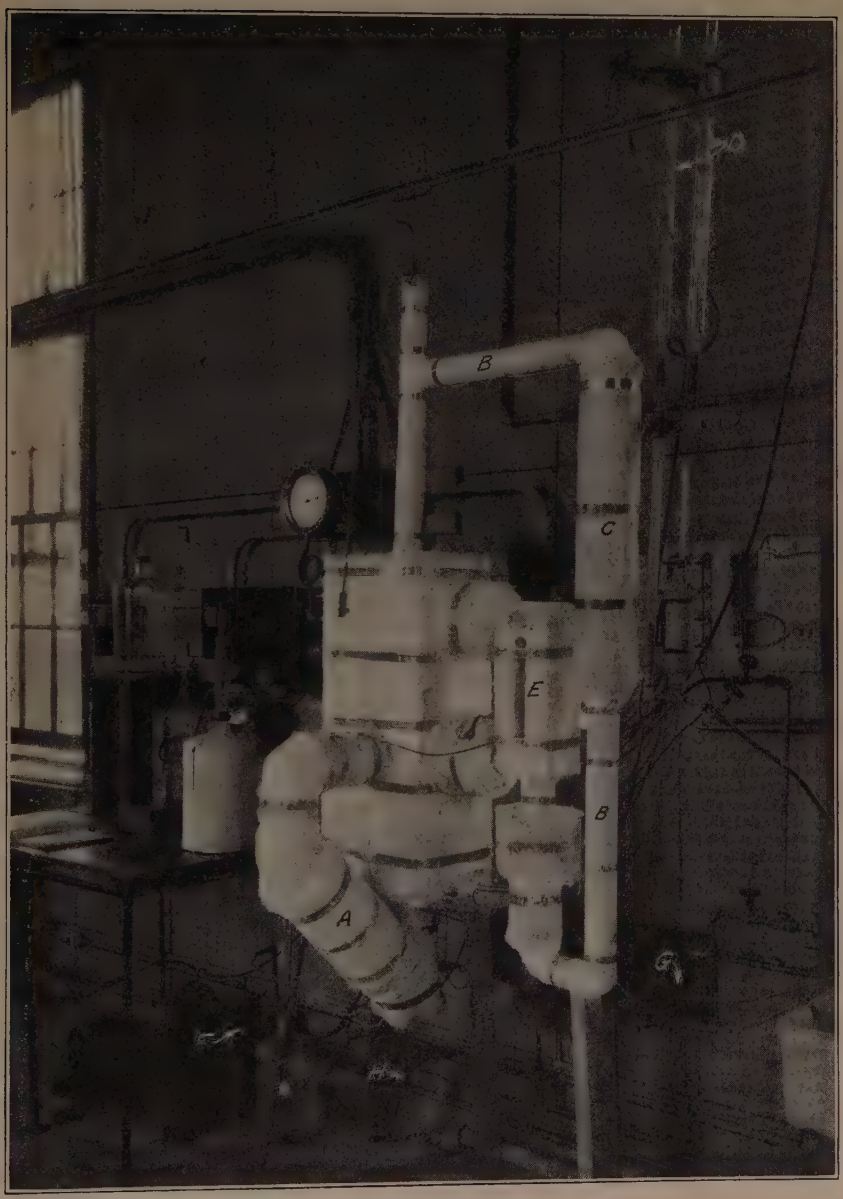

FIG. 15. BOILER USED IN SCALE TEST

FIG. 16. HEATING TUBE FOR BOILER USED IN SCALE TEST

one plunger pumped a feed water of desired composition into the boiler while the other pumped an equal amount of the boiler water out for sampling. In this manner a constant feed could be maintained without changing the volume in the boiler, and thus any desired concentration of chemicals in the boiler could be maintained at any desired period.

The heating tube was made of seamless steel tubing with screw flange unions on each end so that the tube could be removed easily. An iron-constantan thermocouple was inserted and peened in holes drilled in the outer portion of the tube near the center of the heated area. By means of this the temperature of the outer area of the tube was obtained. Another thermocouple inserted in a well gave the temperature of the steam and water as they left the heating tube to enter the drum. A continuous record was made of these two temperatures by means of a multiple-point recording potentiometer. A second thermocouple introduced in the well was connected to a controlling potentiometer which regulated the heat input at the heating tube and maintained a constant temperature in the boiler.

The temperature of the heating wire was over 2000 deg. F. when the rate of heat transfer was high.

The rates of heat transfer through the heating tube were varied between 30 000 and 100 000 B.t.u. per sq. ft. per hr. The heating tube was $^{15}/_{16}$ in. inside diameter and $1^{5}/_{16}$ in. outside diameter, and had an effective heating length of 5 in., and a heating area of 0.102 sq. ft.

The volume of the boiler to the bottom of the gauge glass was 1.3 gallons, and it held 11 lbs. of water at room temperature. The volume to the top of the gauge glass was 2.0 gallons. The rate of steam generation was about 10 lbs. per hr. at 150 lbs. pressure.

22. *Procedure in Operating Laboratory Boiler.* — The boiler was operated under two different conditions: first, adding the feedwater and removing the boiler water continuously, and second, doing this intermittently. When operated according to the first condition the boiler was cleaned out and the desired solid salt introduced into the boiler; a new tube which had been acid-cleaned was put in place, and the boiler was filled with distilled water. The current was then turned on and the boiler heated to the desired temperature. When the boiler was up to temperature, sufficient water was put in the condensing unit to hold the temperature constant. A continuous record was kept of the water temperature and the temperature of the outside of the heating tube. When the boiler had operated for sufficient time to give a record of the difference between the temperature of the outside of the heating tube T_2 and the water temperature on the inside T_1 for distilled water, the pump was started. Distilled water containing the desired concentration of calcium sulphate was then added to the boiler by means of the motor-driven pump. The strokes of the feed and discharge plungers were so adjusted that the water being pumped out of the boiler was equal to that being admitted (about 1.5 lbs. per hr.), and in this manner the water level in the boiler remained constant. As scale formed in the heating tube the temperature difference $T_2 - T_1$ was observed to increase.

At regular intervals samples of the water removed from the boiler were analyzed.

When the boiler had operated for the desired period of time the current was shut off, the blowdown valve G was opened, and the entire contents of the boiler blown out within a few minutes. The tube was then removed for examination. By rapid removal of the boiler water the solid phase on the tube did not have time to change its composition. The flange unions were removed and the tube split

longitudinally into two pieces, thus exposing the scale for examination.

When the feed was intermittent the desired solid phase, either calcium sulphate or calcium carbonate, or both, was added to the boiler before putting the tube in place. When the tube was assembled distilled water containing the desired liquid phase was introduced, and the boiler heated to the desired temperature. Records were kept of $T_2 - T_1$ as in the other tests. Samples of the liquid in the boiler were collected in a steel bomb by sampling into the sealed bomb from the valve H. When the bomb had cooled it was disconnected, and the contents were removed and analyzed.

From time to time the valve G was opened, and the level of the water dropped to the bottom of the gauge glass. The valve was then closed, the pump started (the discharge plunger being disconnected), and sufficient water added to bring the level to the top of the gauge glass. The composition of the water being added varied according to the various tests. At the completion of these tests the boiler was shut down, as in the tests previously reported.

Records were kept in all tests of the energy input into the heating or scaling tube in kilowatt-hours, the rate of heat input in kilowatts, the temperature difference $T_2 - T_1$, the amounts of water being added to and removed from the boiler, the chemical composition of the various solutions, the thickness of the scale produced, and its chemical composition.

23. *Methods of Analysis.*—Analyses were made on the various solutions for hydroxide, carbonate, sulphate and chloride. The hydroxide content was determined by pipetting 50 cc. of the solution into a 200-cc. Erlenmeyer flask to which 10 cc. of a 10-per-cent solution of $BaCl_2$ in CO_2 free water had already been added. The flask was stoppered, let stand 15 minutes, and then titrated with 0.02 N HCl solution to the phenolphthalein end point.

The carbonate was determined by evolving the carbon dioxide from an acidified solution and absorbing it in a standard solution of barium hydroxide. About 400 cc. of the solution was put into a 500 cc. Erlenmeyer flask previously swept clean with carbon dioxide-free air. A stream of carbon dioxide-free air was passed through the solution, through a reflux condenser fitted to the Erlenmeyer flask, through granulated zinc, and finally through a Meyers' sulphur bulb containing 0.02 N barium hydroxide. The solution was acidified, and then heated to boiling, and the air was bubbled through for 20 minutes. After sufficient air had been passed through, the barium hydroxide was washed into a 200-cc. Erlenmeyer flask and titrated with

TABLE 16

RATES OF DECREASE OF SOLUBILITY OF CALCIUM IN $CaSO_4$ AND $CaCO_3$ WITH INCREASE IN TEMPERATURE

Temperature deg. F.	Steam Pressure, lb. per sq. in. gage	Rate of Decrease of Solubility of Calcium in p.p.m. of Calcium per deg. F. temperature increase	
		$CaSO_4$	$CaCO_3$
360	150	0.55	0.10
405	250	0.22	0.05
470	500	0.07	0.02
540	1000	0.05	0.01
600	1500	0.03	0.005

0.02 *N* HCl to the phenolphthalein end-point. The difference between the amount of HCl needed to titrate a volume of barium hydroxide solution before absorption of the carbon dioxide, and that required for a similar volume after absorption, gave a measure of the carbon dioxide. The sodium carbonate in the solution was calculated from the amount of carbon dioxide evolved.

The sulphate was determined by precipitating as barium sulphate and weighing the filtered and ignited precipitate.

The chloride was determined by titration with silver nitrate using sodium chromate as an indicator.

24. *Test Data and Discussion of Results.*—Hall,* as a result of work conducted at Carnegie Institute of Technology, concluded that calcium sulphate, decreasing in solubility with increase in temperature, became less soluble at the heating surface and formed crystals of scale on the heating surface. Calcium carbonate did not form scale according to his theory, since it would become more soluble at higher temperatures, and thus precipitate out as sludge. Partridge† conducted a research at the University of Michigan along lines similar to those Hall had followed and concluded that the rate of scale formation was proportional to the slope of the solubility curve. He predicted that the solubility of calcium carbonate decreased with increase in temperature. Thus, calcium sulphate, decreasing in solubility rather rapidly, would form scale rapidly, while calcium carbonate, decreasing in solubility very slowly, would form scale very slowly.

Figure 17 shows the solubility of calcium sulphate and calcium carbonate as determined in the author's solubility tests. Table 16 gives the rate of decrease of solubility of calcium in parts per million per degree F. for both calcium sulphate and calcium carbonate.

*Hall, R. E., Carnegie Institute of Technology, Bulletin 24 (1927).

†Partridge, E. P., Department of Engineering Research, University of Michigan Bulletin 15 (1930).

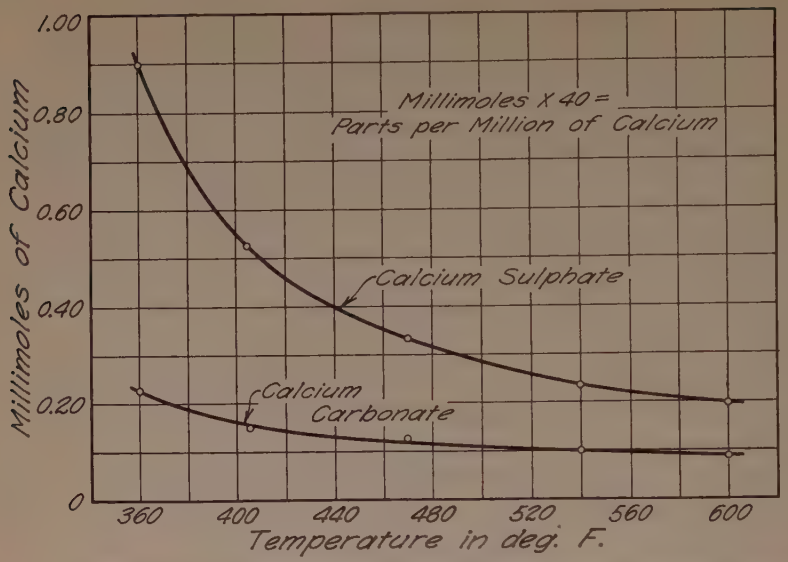

FIG. 17. SOLUBILITY OF CALCIUM, FOR CALCIUM SULPHATE AND CALCIUM CARBONATE

In order to establish the relationship between solubility and rate of scale formation, the boiler was run with a constant rate of heat input at the heating tube, and a solution of calcium sulphate was added to the boiler continuously. Table 17 gives the results of tests run under these conditions at 150, 250 and 500 lb. per sq. in. pressure. The tests at 1000, 1500, 2000 and 2700 lb. per sq. in. pressure, also given in Table 17, were run with solid calcium sulphate in the boiler at the start, and the feed of distilled water was intermittent.

TABLE 17

RATE OF CALCIUM SULPHATE SCALE FORMATION

Test No.	Pressure lb. per sq. in. gage	Rate of Heat Transfer at Heating Tube B.t.u. per sq. ft. per hr.	Total Input to Heating Tube kw.-hr.	Thickness of Scale in.	Rate of Scale Formation in. per kw.-hr. $\times 10^4$	Rate of Scale Formation in. per million lbs. steam per sq. ft.	Solubility of Calcium in Boiler Water p.p.m.
2	150	80 000	425	0.022	0.52	1.45	36
7	250	78 000	356	0.018	0.51	1.35	18
6	500	76 000	368	0.018	0.49	1.20	9
33	1000	70 000	445	0.009	0.20	0.44	5
27	1500	83 000	347	0.008	0.23	0.42	4
36	2000	83 000	224	0.004	0.178	0.26	3
26	2000	83 000	411	0.004	0.10	0.149	3
37	2000	83 000	1416	0.008	0.056	0.082	3
34	2700	83 000	296	0.005	0.17	0.147	2

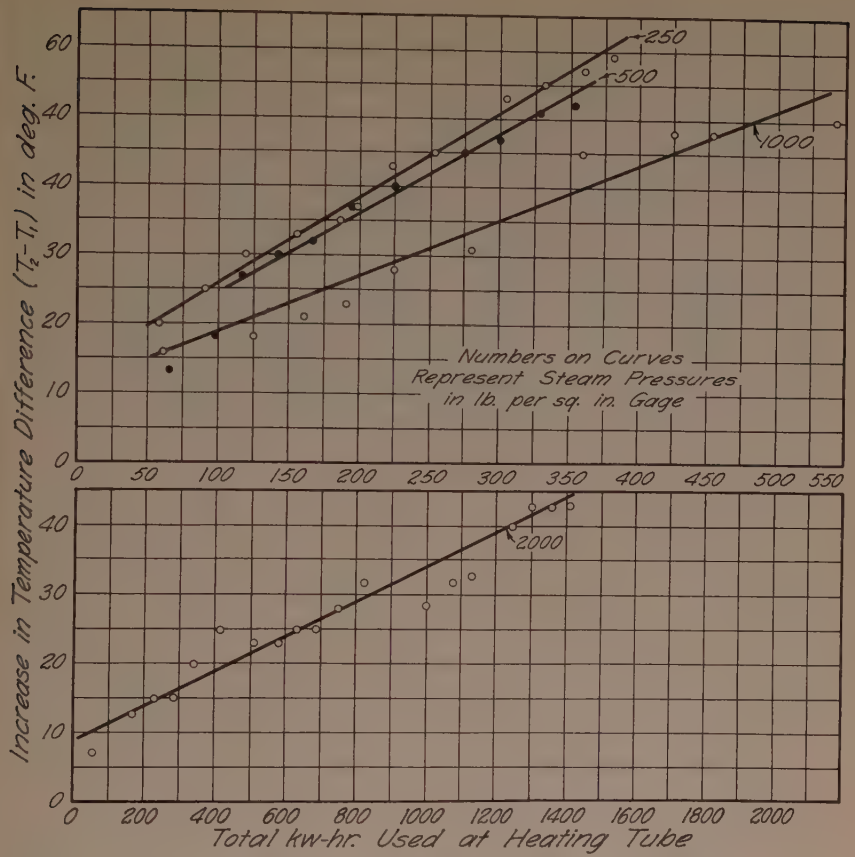
Increase in Temperature Difference (T_2-T_1) in deg. F.
250
500
1000
2000
Numbers on Curves Represent Steam Pressures in lb. per sq. in. Gage
Total kw-hr. Used at Heating Tube

FIG. 18. INCREASE IN TEMPERATURE OF HEATING TUBE DUE TO SCALE FORMATION AT VARIOUS STEAM PRESSURES

The increase in temperature difference $(T_2 - T_1)$ between that at the start and that found after various periods of operation is plotted against the total kw.-hr. input at the heating tube in Fig. 18 for 250, 500, and 1000 lb. pressure. The rate of temperature increase is proportional to the total heat input at the heating tube, and is almost identical at 250 and 500 lb. pressure. The rate of scale formation per kw.-hr. is also almost identical for 250 and 500 lb. pressure. These results would indicate that the scale forms at the same rate at pressures between 150 and 500 lb. per sq. in. It is also evident that the rate of scale formation per pound of steam generated is almost the same at 150, 250 and 500 lb. pressure. Thus, in the test run at 150 lb. pressure, a feedwater containing 250 p.p.m. of calcium sulphate was

fed at the rate of 1.45 lb. per hr. The amount of the calcium ion in the boiler water immediately dropped to an average of 36 p.p.m., which agrees with the solubility data obtained from the bomb tests. The excess calcium compound was thrown out of solution in the boiler proper as fast as it was added. The rate of scale formation was 0.000052 in. per kw.-hr. At 500 lb. pressure a feedwater containing 200 p.p.m. of calcium sulphate was added at a rate of 1.56 lb. per hr. The amount of the calcium ion in the boiler water dropped to 9 p.p.m., again showing that the excess calcium sulphate was thrown out of solution in the boiler. However, the rate of scale formation was almost the same as that obtained at the lower temperatures.

At 1000 lb. pressure the rate of scale formation is much less than at 500 lb. pressure. The rate of temperature increase is proportional to the kw.-hr. input, thus indicating that scale has been forming throughout the test at a fairly constant rate.

At 2000 lb. pressure the rate of scale formation becomes still less. Three tests were run at this pressure, as reported in Table 17. In test No. 36, with 224 kw.-hr. used at the heating tube, a scale 0.004 in. in thickness formed, while in test No. 26, with 411 kw.-hr. used at the heating tube, a scale 0.004 in. in thickness was also formed. A third test was run in which 1416 kw.-hr. was furnished to the heating tube, and a scale of 0.008 in. was formed. The rate of temperature increase for this test (No. 37) is shown in Fig. 18. These results indicate that at this higher pressure a thin scale forms at the beginning of the test, and that the rate of increase in thickness is very slow. Thus, with an input of 224 kw.-hr., 0.004 in. of scale was formed, and with 1416 kw.-hr., only 0.008 in. The rate of increase in thickness of scale, if calculated according to the amount of additional scale formed, would be only 0.033×10^{-4} in. per kw.-hr. at 2000 lb. pressure, which is 6.3 per cent of the rate at 150 lb. pressure, or 6.7 per cent of the rate at 500 lb. pressure. If calculated according to the total scale formed in run No. 37, it would be 0.056×10^{-4} in. per kw.-hr., or 10.7 per cent of the rate at 150 lb. pressure.

The data obtained in the tests reported in Table 17 indicate what factors influence the rate of calcium sulphate scale formation. As already stated, the scale forms from a saturated solution, and is independent within reasonable limits of the rate at which the excess of calcium sulphate is being added. Thus, at 150 lb. pressure the calcium sulphate was being added at the rate of 0.22 lb. per hr. in excess of the solubility, while at 500 lb. pressure it was being added at the rate of 0.34 lb. per hr. in excess; at 1000, 1500, 2000, and 2700 lb. pressure a large excess of solid phase was in the boiler from the start.

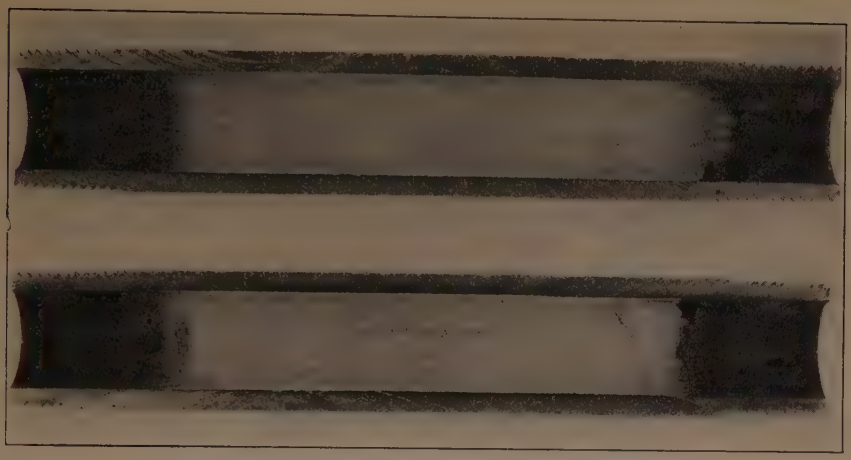

FIG. 19. HEATING TUBE SECTIONED TO SHOW SCALE

Figure 19 shows one of the tubes after sectioning, and illustrates very clearly the manner in which the scale is laid down. The scale is of even thickness for the entire length of the heated area, and then it suddenly stops. This shows that the scale forms on the surface being heated, and but very little forms on the unheated surface. This would indicate that the scale is forming from a saturated solution, and the rate is apparently dependent upon the amount of steam being generated at the heating surface and the amount of calcium sulphate in solution.

Examination of the crystal form of the scale formed at 1000 lb. pressure and lower showed well defined crystals at the extreme ends of the scaled section where the rate of formation was slowest. However, at the center of the tube the crystal growth was so dense that the crystals were not so clearly defined. The definite crystals obtained indicate that the scale is forming by crystallization from a saturated solution, and not by precipitation from a supersaturated solution.

Petrographic examinations* made of samples of scales formed at temperatures up to 540 deg. F. (1000 lb. per sq. in., gage) gave the following results:

The scale is composed of colorless crystals having the following optical properties: biaxial (+); 2 V medium; $\alpha = 1.570$, $\beta = 1.575$; $\gamma = 1.612$; $\gamma - \alpha = 0.042$. These properties are identical with those possessed by the natural mineral anhydrite ($CaSO_4$).

The crystals are prismatic in form, showing two good and one poor cleavage. They belong to the orthorhombic crystal system, and are

*Petrographic examinations were made by Dr. R. E. Grim, Petrographer, Illinois State Geological Survey.

TABLE 18

CHEMICAL ANALYSES OF SCALE FORMED WHEN $CaSO_4$ WAS PRESENT IN BOILER WATER

Test No.	Pressure, lb. per sq. in. gage	Ca per cent	SO_4 per cent	Fe_2O_3 and Insoluble per cent	Unaccounted For per cent	Total per cent
2	150	29.0	72.3	...	−1.3	101.3
6	250	29.0	69.0	1.5	0.5	99.5
7	500	27.0	70.0	2.0	1.0	99.0
33	1000	29.8	68.1	3.5	−1.4	101.4
27	1500	28.4	66.6	3.5	1.5	98.5
26	2000	29.9	59.5	6.2	4.4	95.6
34	2700	28.1	41.0	8.6	22.3	77.7
34S*	2700	28.0	69.2	3.7	−0.9	100.9

*34S—Sludge removed from boiler.

well developed. The individual crystals have a diameter between 0.05 and 0.12 millimeter.

Similar examinations made on scale formed at 2700 lb. per sq. in., gage, showed the material to be composed of very small crystalline particles intimately mixed with a considerable quantity of brown black opaque disseminated material. The size of the individual particle is usually about 0.003 millimeter. The small size of the particles and the presence of the opaque material made the mineral identification difficult or impossible. Most of the crystalline material is definitely anhydrite with the same properties as those possessed by the previous specimens except for the smaller particle size. In addition to the anhydrite, there appears to be present at least one other colorless crystalline constituent. Because of the small size of the particles and the opaque material, sufficient optical data for a definite identification could not be obtained. This material is isotropic, or nearly so, and has an index of about 1.530. Both $CaSO_4 \cdot 2H_2O$ and $CaS_2O_6 \cdot 4H_2O$ are reported to have a range of indices about equal to 1.530 and a low birefringence. There is a suggestion, therefore, that this material may be a hydrated form of $CaSO_4$.

At pressures above 1000 lb. the scale was no longer white and crystalline. It became very dense and black, and the crystalline appearance was not evident. Analyses made on these scales (Table 18) showed that up to 1000 lb. pressure the scale was practically pure calcium sulphate. Above this pressure the sulphate content of the scale became lower. This would indicate that the stable solid phase at the lower temperature was calcium sulphate ($CaSO_4$) without any water of hydration, while at the higher temperature it was a complex salt, being made up of CaO and $CaSO_4$ in varying proportions. The

solid in the boiler water at the higher temperatures was also analyzed. The sludge was found to be calcium sulphate. This indicated that the scale forming at the heating surface at pressures above 1000 or 1500 lb. pressure was changing in composition. At the higher temperature the calcium sulphate is liable to be unstable, forming a complex salt of calcium oxide and calcium sulphate, and the sulphur trioxide released undoubtedly reacts with the iron present. If this is true, one would not expect the scale to be crystalline in form or to deposit at a definite rate. This is apparently what is taking place at the higher temperatures.

25. *Conclusions.*—The conclusions which may be drawn in regard to the formation of calcium sulphate scale are:

(1) The rate of formation of calcium sulphate scale is almost constant at 150, 250 and 500 lb. pressure. At 1000 lb. pressure the scale forms about one-third as fast as it does at 150 lb. pressure (for a constant rate of heat transfer), while at 2000 lb. it forms only about one-tenth as fast as at 150 lb. pressure.

(2) The rate of formation of calcium sulphate scale appears to be independent of the amount of calcium sulphate entering the boiler, or the amount of sludge (within reasonable limits) in the boiler.

V. Scale Prevention in Laboratory Boiler

26. *Procedure in Tests.*—The results obtained in the bomb tests indicated that much lower concentrations of sodium carbonate in the liquid phase were necessary to prevent the formation of calcium sulphate scale than had been previously assumed to be necessary. A few years ago it was assumed that sodium carbonate could not be used above 250 lb. pressure, since the amounts necessary to prevent sulphate scale would give such high alkalinities that the embrittlement ratios could not be maintained. However, the results of the solubility tests indicated that at 1000 lb. pressure a sodium carbonate concentration of 78 p.p.m. would prevent sulphate scale even with the sodium sulphate above 2500 p.p.m. (150 grains per gallon). These data were obtained in bombs which were not generating steam; consequently the partial pressure of the CO_2 in the steam space was high, and the undecomposed sodium carbonate would be high. Thus it was realized that tests must be run under actual steaming conditions in order to be in a position to make this statement with any assurance of its being applicable to power plant operation.

TABLE 19

RUN NO. 12—500 LB. STEAM PRESSURE (470 DEG. F.)
50 GRAMS $CaSO_4$ ADDED TO BOILER AT START; FILLED WITH DISTILLED WATER; INTERMITTENT FEED AND BLOW-DOWN

Sample No.	Time Duration Between Feeding Sample and Blow-down Sample, hr.	NaOH p.p.m.		Na_2SO_4 p.p.m.		Na_2CO_3 p.p.m.		Ca
		Feed	Boiler	Feed	Boiler	Feed	Boiler	p.p.m.
	0.0	180		1550		100		
2	0.25		44		384		23	13
3	2.5		44		450		11	7
	0.0	180		1550		100		
4	0.5		100		830		20	9
5	3.5		105		830		12	9
6	15.5		105		810		8	7
	0.0	180		1550		100		
7	5.0		125		1080		13	8
8	8.0				1040		10	7
9	23.0		122		1080		10	6
	0.0	190		1550		1000		
10	2.0		166		1650		34	6
11	6.0		201		1660		17	6
12	11.0		227		1680		25	7
	0.0	190		1550		1000		
13	12.0		256		2180		31	6
14	16.5		275		2140		28	6
	0.0	190		1550		1000		
15	3.0		246		2410		28	6
16	19.0		280		2370		26	6
	0.0	190		1550		5000		
19	7.0		503		3760		238	2
20	22.5		580		4530		45	3
21	29.5		590		4200		25	2
	0.0	190		1550		5000		
22	20.0		850		4520		644	2
23	37.0		1040		4130		248	1
24	49.0		1080		4940		109	1

Tests were run in the scaling boiler in which a scale of calcium sulphate was formed on the tube, with an excess of calcium sulphate in the boiler as a solid. After sufficient scale had formed a solution of sodium hydroxide, sodium sulphate, and sodium carbonate was fed to the boiler. Samples of water removed from the boiler were analyzed to determine the sodium hydroxide, sodium carbonate, sodium sulphate, and calcium content.

27. *Data from Tests and Discussion of Results.*—The results of these tests are given in Tables 19 and 20.

In run No. 12 at 500 lb. pressure (Table 19) the sodium carbonate in the boiler water was reduced to as low as 25 p.p.m., even with a

TABLE 20

RUN NO. 13—1000 LB. STEAM PRESSURE (540 DEG. F.)
50 GRAMS $CaSO_4$ ADDED TO BOILER AT START; FILLED WITH DISTILLED WATER; INTERMITTENT FEED AND BLOW-DOWN

Sample No.	Time Duration Between Feed and Taking Sample, hr.	NaOH p.p.m.		Na_2SO_4 p.p.m.		Na_2CO_3 p.p.m.		Ca
		Feed	Boiler	Feed	Boiler	Feed	Boiler	p.p.m.
	0.0	0		0		0		
3	90.0		15		12		3.8	11
4	112.0		18		14		7.8	11
5	134.0		20		11		5.5	11
	0.0	197		1550		100		
7	6.5		160		270		20.0	3
8	22.0		240		238		14.0	2
	0.0	197		1550		100		
9	8.0		254		483		27.0	4
10	24.0		304		583		23.0	2
	0.0	197		1550		100		
11	8.0		308		845		21.0	3
	0.0	296		1550		1000		
12	13.0		425				31.0	
	0.0	296		1550		1000		
13	7.5		390		1615		28.0	5
	0.0	296		1550		1000		
14	15.0		485		1675		31.0	4
	0.0	425		1550		5000		
15	6.0		1020		2560		187.0	3
16	21.0		1200		3140		47.0	3
	0.0	425		1550		5000		
17	24.0		1840		4110		138.0	0

feedwater containing 1000 p.p.m. of sodium carbonate, within three hours after the addition of the feed water, and at the same time the sodium sulphate was 1600 p.p.m. When a feedwater of 5000 p.p.m. of sodium carbonate was added to the boiler the soda ash content was not reduced so fast. However, calculation showed that at this point practically all the calcium sulphate had been converted to sodium sulphate and calcium carbonate.

In run No. 13 at 1000 lb. pressure (Table 20) the sodium carbonate content in the boiler water was reduced to practically the same figure as at 500 lb. pressure.

These results indicate that it is possible to maintain sufficient sodium carbonate at 1000 lb. pressure to prevent calcium sulphate scale even when the sodium sulphate content is over 1700 p.p.m.

At the completion of these runs the heating tubes, when examined, showed that the scale was on the tube in two distinct layers. The

top layer was a thin black scale which could be readily removed from the lower layer. It was magnetic, and appeared to contain appreciable quantities of magnetic iron oxide. The scale next to the tube was a hard white crystalline scale similar to the regular calcium sulphate scale. The scale was breaking loose from the heating tube at several places. Analyses of the two distinct layers of scale in the two tubes gave the following results:

Results of Analyses of Boiler Scales in Per Cent Composition

Scale No	12	12	13	13
Location	Lower	Top	Lower	Top
Ca	24.5	28.9	27.1	31.0
SO_4	63.3	16.5	64.4	11.9
CO_3	4.4	40.5	6.8	47.3
Fe_2O_3	2.0	15.2	1.2	5.1
Undetermined	5.8	0.0	0.5	4.7

These results show that calcium sulphate scale was formed first, and the sodium carbonate reacted with the top portion of this scale to change it to calcium carbonate, which protected the lower portion of calcium sulphate from further attack. This would indicate that the removal of calcium sulphate scale by means of soda ash treatment would be rather slow. However, a study of the increase of $T_2 - T_1$ during these two runs showed that as soon as the sodium carbonate content became greater than 25 p.p.m. in both runs the temperature difference remained constant, indicating that scale was no longer forming. This would indicate that a concentration of 25 p.p.m. (1½ grains per gallon) of sodium carbonate in the boiler, even at 1000 lb. pressure, will prevent calcium sulphate scale formation, even when the sodium sulphate content is greater than 3000 p.p.m. (175 grains per gallon).

In order to determine the limiting value of sodium carbonate more definitely, a study was made of the reaction, starting with calcium carbonate in the boiler and adding a solution of sodium sulphate and sodium hydroxide.

Table 21 gives the results of a test conducted at 540 deg. F. (1000 lb. pressure) in which calcium carbonate was put into the boiler, and a solution containing sodium hydroxide and sodium sulphate was used as a feedwater. The sodium carbonate content of the boiler water increased to between 20 and 30 p.p.m. and appeared to stay there. The sodium hydroxide content remained at between 400 and 500 p.p.m. The sodium sulphate content was maintained around 4000 p.p.m.

TABLE 21

RUN NO. 16—1000 LB. STEAM PRESSURE (540 DEG. F.)
50 GRAMS $CaCO_3$ ADDED TO BOILER AT START;
INTERMITTENT FEED AND BLOW-DOWN

Sample No.	Time Duration Between Feed and Taking Sample, hr.	NaOH p.p.m.		Na_2SO_4 p.p.m.		Na_2CO_3 p.p.m.		Ca
		Feed	Boiler	Feed	Boiler	Feed	Boiler	p.p.m.
1	0	180		1550		11		0
	18		330		1330		21	0
2	0	180		1550		11		0
	6		288		1420		27	0
3	23		352		1370		18	0
4	30		384		1340		16	0
5	47		427		1280		17	0
6	0	180		3040		18		0
	7		352		1980		17	0
7	24		380		1980		23	4
8	47		445		1970		18	4
9	0	180		6150		18		0
	24		400		3680		21	4
10	48		456		3750		19	4
11	72		493		3880		26	4
12	0	194		3630		10		0
	24		436		4000		21	4
13	48		485		4120		13	4
14	0	194		3630		10		0
	24		420		4110		26	4
15	52		468		4300		26	4
16	0	194		3630		10		0
	21		410		4150		27	4
17	45		460		4370		29	4
18	0	194		3630		10		0
	24		405		4340		18	4

(230 grains per gallon). The sludge remaining in the boiler at the completion of this test had 37.5 per cent carbonate present or 62 per cent calcium carbonate, thus showing that calcium carbonate as a solid phase was stable in the presence of sodium sulphate when the sodium sulphate was over 4000 p.p.m. and the sodium carbonate not over 30 p.p.m.

The reactions involved in these studies are as follows:

$$(1)\quad CaSO_4 + Na_2CO_3 \leftrightarrows Na_2SO_4 + CaCO_3$$
$$(2)\quad Na_2CO_3 + H_2O \rightleftarrows 2NaOH + CO_2$$

If calcium sulphate is the solid phase at the beginning of the tests as in run No. 13 (Table 20) and a solution containing sodium carbonate is added, the sodium carbonate will react to form sodium sulphate and calcium carbonate. However, the reaction (1) is reversible, and if the sodium carbonate becomes less than the amount required to force the

TABLE 22

TEST RUN AT 1000 LB. STEAM PRESSURE (540 DEG. F.)
$CaCO_3$ AND $CaSO_4$ ADDED TO BOILER AT START

Feed	Total Input to Heating Tube kw.-hr.	Composition of Feed Water, p.p.m.				Composition of Boiler Water, p.p.m.				Ratio $\frac{Na_2SO_4}{NaCl}$	
		NaCl	Na_2SO_4	NaOH	Na_2CO_3	NaCl	Na_2SO_4	NaOH	Na_2CO_3	Feed	Boiler
Intermittent	61	62	495	51	12	62	222	138	11	8.0	3.6
	125	62	495	51	12	62	183	165	11	8.0	2.9
	223	62	495	51	12	62	110	173	12	8.0	1.8
	411	62	495	51	12	62	62	178	10	8.0	1.0
Continuous	431	62	495	0	56	62	194	139	17	8.0	3.1
	495	62	495	0	56	63	380	100	21	8.0	6.0
	537	62	495	0	56	62	430	77	26	8.0	6.9
	550	62	495	0	56	63	372	75	22	8.0	5.9
	620	62	495	0	56	62	483	62	31	8.0	7.8
	659	62	495	0	56	63	542	16	74	8.0	8.6
	676	62	495	0	56	62	485	77	21	8.0	7.8
	725	62	495	0	56	62	435	64	20	8.0	7.0
	742	62	990	0	56	62	695	73	22	16.0	11.2
	790	62	990	0	56	63	920	73	25	16.0	14.8
	850	62	990	0	56	63	865	42	24	16.0	14.0
	910	62	990	0	56	62	1010	53	20	16.0	16.3
	971	62	990	0	56	62	950	48	21	16.0	15.3
	982	62	990	0	56	63	990	32	23	16.0	16.0
	1028	62	990	0	25	62	1020	67	19	16.0	16.5
	1103	62	990	0	25	62	960	67	23	16.0	15.5
	1150	62	990	0	25	62	840	62	15	16.0	13.5
	1164	62	990	0	25	63	900	64	14	16.0	14.3
	1207	62	990	0	15	62	860	59	15	16.0	13.8
	1273	62	990	0	15	74	1020	69	15	16.0	13.8
	1337	62	990	0	15	84	1020	40	14	16.0	12.2

reaction to the right, the reaction will proceed to the left. Thus, if calcium carbonate is used as a solid phase, as in run No. 16 (Table 21), and sodium sulphate is added, sodium carbonate and calcium sulphate will be formed. The sodium carbonate will tend to react according to reaction (2).

The results tabulated in Tables 20 and 21 indicate that the amount of soda ash required to prevent the formation of calcium sulphate is about 25 p.p.m., and this amount should be effective with the sodium sulphate as high as 3000 p.p.m.

It was desirable to check still further the amount of carbonate necessary to prevent calcium sulphate formation as a stable phase in the boiler. The procedure followed was to add calcium carbonate and calcium sulphate to the boiler, and then fill with a solution containing definite amounts of sodium hydroxide, sodium chloride, sodium carbonate, and sodium sulphate. If the carbonate content was too low, the sulphate would precipitate and lower the sulphate content of the solution. Thus, if samples removed from the boiler showed no loss of sulphate, calcium sulphate was not forming, and the carbonate content present would be sufficient to prevent calcium sulphate formation. The

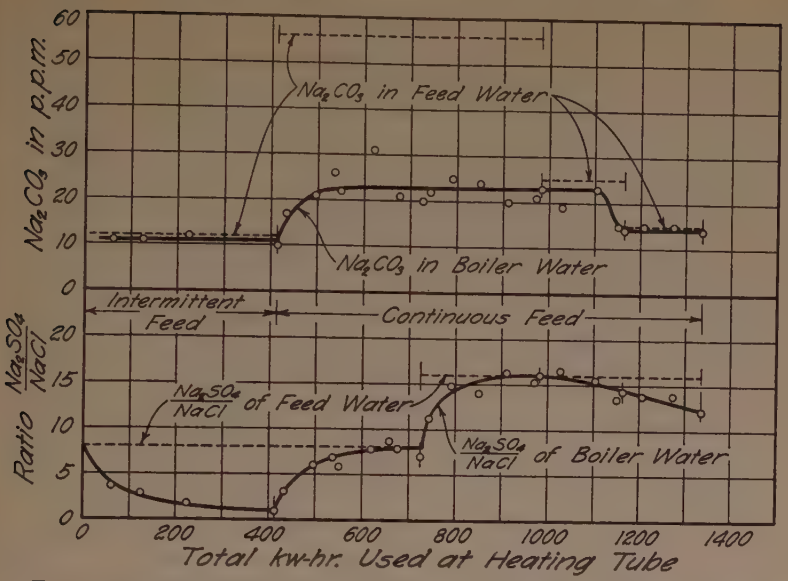

FIG. 20. Na_2CO_3 CONTENT AND $Na_2SO_4/NaCl$ RATIO FOR BOILER WATER, FOR 1000-LB. STEAM PRESSURE, INTERMITTENT AND CONTINUOUS FEED

chloride present, since it does not enter into any reaction, would serve as a measure of concentration if any took place. Thus, if the $\frac{Na_2SO_4}{NaCl}$ ratio of the water in the boiler was the same as that of the water being added, no calcium sulphate was forming, while if this decreased, calcium sulphate was forming. The test was run first with intermittent feed, feeding only sufficient water to make up for that removed for the analyses, and second, with a continuous feed. The results of the tests run at 1000 and 2000 lb. pressure are given in Tables 22 and 23; the results of the 1000 lb. test are also presented in Fig. 20, which shows that at 1000 lb. pressure (540 deg. F.), with intermittent feed, the sodium sulphate—sodium chloride ratio decreased rapidly, and the sodium carbonate content remained about 10 p.p.m. When the continuous feed was started feeding at the rate of 1 lb. per hr. with a solution having 50 p.p.m. sodium carbonate present, the $\frac{Na_2SO_4}{NaCl}$ ratio increased to a value equal to that of the solution being added. The sodium carbonate content increased to around 25 p.p.m. The $\frac{Na_2SO_4}{NaCl}$ ratio of the feedwater was then raised, and that in the boiler also increased to the same figure, and the sodium carbonate content remained around 25 p.p.m. The sodium carbonate content of

TABLE 23

TEST RUN AT 2000 LB. STEAM PRESSURE (640 DEG. F.)
$CaCO_3$ AND $CaSO_4$ ADDED TO BOILER AT START

Feed	Total Input to Heating Tube kw.-hr.	Composition of Feed Water, p.p.m.				Composition of Boiler Water, p.p.m.				Ratio $\frac{Na_2SO_4}{NaCl}$	
		NaCl	Na_2SO_4	NaOH	Na_2CO_3	NaCl	Na_2SO_4	NaOH	Na_2CO_3	Feed	Boiler
Intermittent	...	62	495	51	9	..	...	...	..	...	...
	42	62	495	51	9	..	...	...	..	...	...
	104	62	218	51	9	77	218	294	12	8.0	2.8
	122	62	182	51	9	78	182	288	19	8.0	2.3
	168	62	179	51	9	71	179	277	20	8.0	2.5
	296	62	158	51	9	71	158	264	23	8.0	2.2
Continuous	112	62	990	0	45	62	940	56	23	16.0	15.2
	180	62	990	0	45	62	910	37	30	16.0	14.7
	237	62	990	0	45	63	900	38	28	16.0	14.3
	275	62	990	0	45	63	1020	42	27	16.0	16.2
	301	62	990	0	65	63	1010	40	32	16.0	16.0
	344	62	990	0	65	63	910	43	24	16.0	14.5
	365	62	990	0	65	63	960	37	33	16.0	15.3
	402	62	990	0	100	63	975	45	36	16.0	15.5
	452	62	990	0	100	62	1055	80	37	16.0	17.0
	505	62	990	0	100	62	1010	65	40	16.0	16.3

the feed water was lowered to 25 p.p.m., and the $\frac{Na_2SO_4}{NaCl}$ ratio started to decrease. The feedwater sodium carbonate content was then lowered to 15 p.p.m. and the sodium carbonate in the boiler dropped to around 15 p.p.m., and the $\frac{Na_2SO_4}{NaCl}$ ratio of the boiler water continued to decrease.

These results indicate that the sodium carbonate content necessary to prevent the formation of calcium sulphate as a stable phase in the boiler at 1000 lb. pressure is about 25 p.p.m. and independent of the sulphate content (at least in the range tested).

Similar tests were run at 2000 lb. pressure. The results are given in Table 23. When the intermittent feed was used, the $\frac{Na_2SO_4}{NaCl}$ ratio decreased in value very rapidly, and the sodium carbonate content remained about 20 p.p.m. When the continuous feed was used, and the sodium carbonate was above 40 p.p.m. in the feedwater, the $\frac{Na_2SO_4}{NaCl}$ ratio remained almost constant, indicating that the calcium sulphate was not forming. The sodium carbonate in the boiler water increased to about 30 p.p.m. When the sodium carbonate content in the feedwater was raised to 100 p.p.m., the $\frac{Na_2SO_4}{NaCl}$ ratio increased and the

sodium carbonate content also increased, indicating that the calcium sulphate in the boiler was being converted to calcium carbonate. This indicated that if the sodium carbonate content is above 30 p.p.m., calcium sulphate will not form as a stable phase at 2000 lbs. pressure.

The results of the tests conducted in the scaling boiler check very closely the results obtained in the bomb tests. These results in the boiler test were obtained by running the tests under three different conditions. Thus, by adding calcium sulphate to the boiler and then feeding a solution of sodium carbonate, sodium hydroxide and sodium sulphate, it was found that the amount of sodium carbonate necessary to prevent calcium sulphate formation as a stable phase was around 25 p.p.m. at 1000 lb. pressure. When calcium carbonate was used as a solid and the equilibrium approached from the opposite side, it was found that about 25 p.p.m. of sodium carbonate was also necessary at 1000 lb. pressure. When calcium sulphate and calcium carbonate were both present and a continuous feed of a solution containing sodium carbonate, sodium hydroxide, sodium sulphate, and sodium chloride was used, it was found that 25 p.p.m. of sodium carbonate was also the critical concentration at 1000 lb. pressure. From these results it appears evident that if a concentration of sodium carbonate greater than 30 p.p.m. is maintained in the boiler water at all times, calcium sulphate scale should be prevented even at pressures as high as 2000 lb. per sq. in.

28. *Conclusions.*—The following conclusions may be drawn:

(1) The presence of more than 30 parts per million (1.7 grains per gallon) of sodium carbonate in the boiler water will prevent the formation of calcium sulphate scale at pressures up to 2000 lb. per sq. in.

(2) The carbonate content necessary to prevent sulphate scale is independent of the sulphate concentration within the limits of concentrations carried in the average high-pressure boiler.

VI. Scale Prevention In Industrial Power Plants

29. *Results of Actual Tests.*—The actual test of the value of the data collected as a result of the tests already reported is, in the final analysis, their application to actual steam boiler operation. Samples of boiler waters have been collected from a large number of power plants operating at various pressures and with various types and amounts of make-up water, systems of water treatment, etc. These samples have been analyzed in order to study the actual concentra-

TABLE 24

ANALYSES OF BOILER WATERS FROM PLANTS NOT HAVING SCALE DIFFICULTIES

Plant	A	B	C	D	E	F
Pressure, lb. per sq. in.	160	225	250	450	400	700
NaOH, p.p.m.	200	90	247	275	144	103
Na_2CO_3, p.p.m.	26	29	64	50	42	8
Total Alkalinity, p.p.m.	291	148	402	415	233	144
Na_2SO_4, p.p.m.	3100	5030	775	1271	3350	1130
NaCl, p.p.m.	125	692	...	....	1240	190
$\frac{Na_2SO_4}{\text{Total Alkalinity}}$	10.6	34.0	1.93	3.08	14.4	7.8
$\frac{CO_3}{SO_4}$	0.007	0.0047	0.0685	0.0326	0.01	0.01
Per Cent Makeup	10	20	90	20	20	2
Hardness of Makeup Water, p.p.m.	50	290	10	10	10	2

tions of the various dissolved solids. The results of the analyses of a typical group of boiler waters covering a wide range of operating pressures and percentages of make-up are given in Table 24.

These plants were all classed as potentially scale-forming under the older theories. The operators at Plants C, D, E, and F were advised to use the phosphate treatment for the prevention of scale. However, these plants have all shown at least one year's (and one over five year's) operation free from scale without using the phosphate treatment. These results appear to check the results obtained in the laboratory research.

Before applying the results of the laboratory work directly to plant operation, the operators should realize that a thorough knowledge of their particular conditions of operation, type of water, and methods of analysis is essential. The laboratory results show the amount of sodium carbonate which must be maintained in the boiler water to prevent sulphate scale, but they do not say that this amount is stable in the boiler water. The results in Chapter III show that in instances where an appreciable percentage of make-up is being added and a small amount of soda ash is being fed continuously, the residual soda ash in the boiler should be sufficient to prevent scale. However, the intermittent feeding of soda is not to be recommended due to the high rate of decomposition in the boiler.

The actual measure of the sodium carbonate present is, of course, obtained from the analyses of samples of the boiler water. It has

been found that the titration method of analysis gives only a rough measure of the sodium carbonate present, and, unfortunately, when it is low, the reported results are high. With the sodium carbonate content below 150 p.p.m. by the regular phenolphthalein and methyl orange titration on a clear water, the actual sodium carbonate may be as low as 50 p.p.m. Consequently, it would be advisable for each plant to have the carbonate content checked from time to time by the accurate Evolution method. Several plant operators have found, as a result of numerous check analyses, that in each particular plant the sodium carbonate determined by titration may be multiplied by a factor to give the actual carbonate with a sufficient degree of accuracy.